EFFECT OF ULTRASONICS ON PHOTOGRAPHIC FILMS

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A C K N O W L E D G E M E N T

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INTRODUCTION

An up-to-date review on the techniques of ultrasonography and on the theories of its mechanism is given in the beginning of this chapter. This is followed by a brief description of the photographic emulsion, Gurney-Mott theory of latent image formation in it and ultrasonic phenomena like radiation pressure, cavitation and sonoluminiscence which can influence this image formation. The contradictions in the theories on the mechanism of ultrasonography and various experiments carried out in this investigation to understand this mechanism are given at the end of this chapter.

1.1 ULTRASONOGRAPHY

When a photographic film is exposed to light a latent image is formed on it which becomes visible on development. In 1933, Marinesco[1] observed that a latent image can also be formed on a photographic film if it was moistened and exposed to ultrasonic waves and in 1951, Ernst[2] suggested certain nomenclature for these images bearing strict analogy to corresponding terminology in optics. Any material which changed recognisably under the influence of ultrasonics was called a sonosensitive material. The production of visible image by means of ultrasonics was called ultrasonoscopy and that of a recorded image was called ultrasonography. He designated the recorded images as ultrasonographs and the instruments for making these images as ultrasonographic cameras.

Ernst[2] obtained ultrasonographs of axial longitudinal section of the amplitude field in front of a circular quartz transducer using special silver bromide plates and proved their importance in research and in medical diagnosis. In 1959, Keck[3] obtained some well resolved ultrasonographs of metallic specimens by immersing coloured films in dilute developer and exposing them to parallel and perpendicular ultrasonic radiation. In 1960, Dehn[4] obtained interference patterns in the near field of a circular piston transducer on photographic papers immersed in dilute developer. These

patterns were well defined and were used to confirm the predictions of the wave theory on the variation of the intensity of the interference pattern of the waves emitted by a circular piston.

The intensity of ultrasonic waves in these experiments was of the order of 1-5 watts/cm^2, and exposure time was 10 to 60 minutes. Obviously the usefulness of these ultrasonographs will greatly increase if they could be obtained in a very short exposure time using low intensity waves. It is hoped that quite soon ultrasonography will greatly supplement X-ray radiography and thus be a boon to industry and medical diagnosis.

1.11 THE TECHNIQUES OF ULTRASONOGRAPHY:

In 1933, Marinesco[1] obtained ultrasonographs on moistened photographic plates immersed in CCl_4. He could not obtain images on dry plates and he could obtain better images if the plates were immersed in dilute developer rather than in CCl_4.

In 1951, Bennett[5] described a new method of obtaining ultrasonographs in which he immersed starch plates in dilute solutions of iodine. The region exposed to ultrasonic waves got blackened due to enhanced chemical action of iodine on

starch. This method gave better diffraction patterns and had the advantage of not requiring dark room processing. But the images thus obtained faded after some days. In the same year Ernst and Hoffman[6] tried temperature sensitive chromotropic substances, temperature sensitive phosphors etc. to record ultrasonic images. They concluded that the method using phosphors gave satisfactory results for an exposure time of only three minutes, and was capable of future improvement.

In 1962, Peterman[7] described a technique in which ultrasonic waves of frequency 3 Mc/s and intensity 0.1 to 0.6 watts/cm^2 produced changes in a phosphorescent material which could be used to obtain an image. The ultrasonic beam was absorbed in the dark by a Ca-SrS phophorescent plate irradiated by a mercury vapour lamp. The plate was quickly applied on a panchromatic emulsion in total darkness. The decay of phosphorescence was more rapid at higher temperatures and the blackening of the image thus formed was proportional to the intensity of the ultrasonic waves. Though the exposure to ultrasonic waves was for less than a minute the method has the disadvantage of requiring dark room processing

In 1967 Schilb[8] et el suggested a bleach out method to obtain ultrasonographs. They obtained images by exposing photographic plates soaked in a dye and immersing it in aqueous solution of the bleach in open light. The action

of the bleach on the dye occurs at a rate depending on the intensity of ultrasound. The result is a permanent negative of the field. In 1962 Berger and Kraska[9] suggested a method in which they immersed commercially available photographic films in water-iodine solutions instead of starch plates. But the exposure time using commercial films was larger than the one using starch plates.

Ultrasonic images are today best obtained using electronic methods described by Suckling[10] and others. In this, ultrasonic waves after transmission through the portion of the body whose image is required, are converted into electric signals and displayed on an oscilloscope.

But a sonosensitive system that can replace X-ray radiography is yet to be found. The electric system is too complicated to be used commercially. The sonographic methods require too long a time of exposure and the intensity of the incident waves is too large for the safety of the exposed tissues and besides they require complete dark room processing. Furthermore, the mechanism of ultrasonography is not clearly understood.

1.12 THE MECHANISM OF ULTRASONOGRAPHY:

Marinesco and his co-workers could obtain an image only if the plate was premoistened in water. They compared

this with the latent image formation on photographic emulsion by shock-waves produced by the explosion of mercury fulminate. In the later case too an image could be obtained only on a moist emulsion. They also observed that the adiabatic temperature rise in the compressed regions of the transmitting liquid, namely water was of the order of $0.01^{\circ}C$ and zero at $4^{\circ}C$. The fact that an image could be produced even at $4^{\circ}C$ with water as transmitting medium and even otherwise this small rise in temperature is insufficient to produce a latent image led them to conclude that image formation is not due to thermal effects. They were of the opinion that the latent image formation is due to the activation of the silver halide crystals by shock excitation produced by the mechanical action of the ultrasonic waves.

Marinesco[11] et el also exposed photographic plates for different time intervals and in different liquids. The density exposure curve resembled Driffield and Hurter characteristic curve for the photographic emulsion. The images were better when the emulsion was immersed in developer rather than in water. They also exposed a photographic film pre-exposed to ultrasonics to light and observed alternation of light and dark bands. They were therefore of the opinion that pre-exposure to ultrasound makes the film more sensitive to light.

In 1947, Pinoir and Pouradier[12] reported that their experimental results proved in a positive fashion that ultrasonics had no direct action on the emulsion producing the latent image. They held that latent image was due to sonoluminiscence. Their conclusions were as follows: (1) Both, luminiscence which was visible to the dark adapted eye and latent image disappeared when the ambient pressure was reduced to 15 cm.Hg. (2) when tetrazine which is known to have no action on the emulsion, was added to water to suppress luminiscence, latent image was also likewise suppressed. (3) Marinesco obtained his sharpest pictures on soaked plates immersed in CCl_4 and it is known that addition of a few drops of CCl_4 to water enhances sonoluminiscence. (4) When the above experiments were repeated in dilute developer the reduction of pressure or addition of tetrazine reduced the image but did not suppress it and this they attributed to the action of ultrasonics on development and to some chemical action.

In 1948, Polotoskii[13] studied the variation in the density of blackening with the intensity of sonoluminiscence. He observed that when the ambient atmospheric pressure was 114 cm, 76 cm, 38 cm and 10 cm of Hg the corresponding density of blackening was zero, 0.11, 0.08 and zero respectively. He also observed that both cavitation and intensity of sonoluminiscence decrease at high and at low pressures. Obviously, these

results support the theory that blackening is due to sonoluminiscence.

In 1953 Benott[14] strongly supported Marinesco's direct action theory. He observed that (1) Even when the ambient pressure was reduced to 2.5 cm Hg, images were formed on the films. (2) The density of blackening increased with the increase in temperature in the temperature range 20-26°C and since sonoluminisicence intensity was known to decrease with the increase in temperature[15] he observed that the above result contradicted sonoluminiscence theory of image formation. (3) Images were obtained on films with different tungsten speed in the range 8 to 160 ASA but the density of blackening remained nearly the same and if blackening was due to luminiscence he argued then the density on films of higher speed should have been more.

In conclusion he wrote that his results have led him to strongly oppose the sonoluminiscence theory and to support the direct action theory. In 1960, Dehn[4] too has supported the view that image formation is due to direct action of ultrasonics.

In 1963, Arkangelskii[16] studied the fogging of photographic plates immersed in water and in developer in the presence and absence of ultrasonic irradiation. He observed

that on the onset of cavitation, the latent image is formed by sonoluminiscence even if the exposure is only for a few minutes. But if the intensity of ultrasonic waves is below the threshold of cavitation an image can only be obtained in a developer and that too for prolonged exposures. The image formation in the absence of sonoluminiscence, he concludes, is due to the acceleration of fogging. Again in 1966, in a review paper Arkangelskii[17] has expressed his view that image formation is probably a secondary effect. However he has not considered the results reported by Bennett and has finally concluded that the mechanism of the action of ultrasonic waves on development of the image in photographic materials is still a problem.

1.2 IMAGE FORMATION IN PHOTO-EMULSIONS

The photographic emulsion[18] is a mixture of silver halide, silver sulphide, colloidal silver and gelatin. Negative emulsion used to record the image consists of silver bromide with a small percentage of silver iodide. Positive emulsions used for the development of the image consists of silver chloride or a combination of silver chloride and silver bromide. The crystals in the emulsions vary in size from submicroscopic to a maximum of 3 to 6 microns and constitute 30 to 40% of the total weight of the emulsion. Although both silver bromide and silver chloride crystalline in cubic structures, the crystals of an emulsion vary considerably in shape from flat triangular or hexagonal tablets to long needle-like forms and almost spherical shapes. The average crystal size is larger for negative emulsions than for positive ones. Similarly the average crystal size is larger for emulsions which have higher speed values, i.e. which are more sensitive to light. Each crystal acts as an individual unit in exposure and development except when in actual contact with one another.

The gelatin is more than a medium to hold the crystals in place on glass, film or paper base. It serves to regulate the sizes of the crystals formed when silver halide

is precipitated from solutions of silver nitrate and a halide such as potassium bromide. It often contributes to the sensitivity of the crystal to light by containing sensitivity promoting chemicals. Gelatin is not a sharply defined chemical. It belongs to the protein group, the molecules being made up of amino acid residue in chains. The connection being between the acidic group of one amino group and basic group of the adjoining one. It has got both acidic and basic properties. When dry gelatin is placed in water it swells; the amount of swelling depending upon the PH and the salt content of water. The swollen gelatin is soft and is easily penetrated by solutions containing small sized molecules, such as the developer. At temperature of about 40° ^{o}C it becomes a solution in water.

Latent Image:

In most emulsions the tiny silver halide grains store up the effect of an exceedingly small amount of light. The store-up effect of light is known as the latent-image. The phenomenon of latent image formation in photo-emulsions is not yet clearly understood. Many hypotheses have been put-forth in this connection and the one that is at present commonly accepted was put.forth by Gurney and Mott.[19] They used the following concepts:

1. The lowest energy level in a conduction band of silver bromide is higher than lowest filled level in the conduction band of metallic silver. Therefore an electron passing from silver bromide to a speck of silver gives up a small amount of energy and gets trapped.

2. A perfect silver halide crystal would contain uniform spacing of Ag^{+} and Br^{-} ions. But in many cases, crystals contain some ions which are not in the proper place but in terstitual positions.

3. Silver bromide contains particles of colloidal silver.

4. There are sensitivity specks probably silver sulphide, in a silver halide. These specks too can trap electrons in the conduction band of the silver halide crystal.

They then gave the following hypotheses. When silver halide crystals are exposed to light some electrons are elevated to higher conduction band and on wandering around come in contact with a speck of silver and get trapped. This charges the speck negatively and so the speck will attract some of the interstitual ions of silver and neutralise them

to form silver atoms which get attached to the speck already present. It is reasonable to assume that latent image consists of metallic silver and this silver is located in patches in or on the grain.

Development: The latent image can be multiplied manifold by the action of the developer. The development of photographic latent image is essentially the reduction of grains of exposed silver halide to metallic silver. During normal development only exposed grains containing a latent image are reduced. If development is extended over a long enough period of time all grains are developed. The development of the latent image is a rate phenomenon, the development of the exposed grains taking place at a greater rate than the development of unexposed grains.

Fixing: The removal of the silver halide grains remaining after development requires two operations, (1) fixing,- the conversion of the silver halide into water soluble compounds. Although there are a number of solvents of six silver halide, sodium thiosulphate (Hypo) is commonly used as a fixing agent. "Washing"removes the soluble silver thiosulphate, hypo and other substances present in the emulsion leaving out silver in the exposed region. Thus on developing, fixing and washing a latent image is converted into a permanent image.

Density of the Image: The amount of x the photographic image produced by exposure and development may be stated in terms of (a) the mass of the silver per unit area and (b) the absorption of light by the image. Since the analytical determination of the mass of silver is laborious in practice the measurement of the image is accomplished by a determination of absorption of light. Hurter and Driffield[20] defined density D as the number of particles of a substance spread over a unit area A, multiplied by the coefficient of absorption K, i.e. $D = K.A$. In its applications to negatives the density is taken to be directly proportional to the amount of silver deposited per unit area and is used as a measure of that amount.

1.3 ULTRASONIC WAVES:

Ultrasonic waves are mechanical waves whose frequency ($\geq$ 20 Kc/s) is beyond the limit of human hearing. They propagate rectilinearly and in general, they may be considered to be plane-waves. While propagating, an ultrasonic beam suffers very little divergence. Their velocity is very small compared to that of electromagnetic waves, the order of magnitide of the velocity of later is 10^{10} cm/sec and that of the former is 10^{3} cm/sec. They undergo reflection, refraction diffraction, scattering interference etc., and they can be focussed to a point.

While propagating through liquids ultrasonic waves produce (1) thermal effects; (2) hydrodynamic effects such as acoustic streaming and microstreaming; (3) radiation pressure and (4) cavitation which produces chemical changes and sonoluminiscence. One or more of these phenomena may be responsible for the blackening of photoemulsions by ultrasonics.

The thermal effect is due to absorption of ultrasonic energy by the transmitting liquid or by the photo-emulsion. This produces a change in temperature of only a few degrees centigrade. The phenomenon of acoustic streaming usually gives rise to forward motion of the liquid molecules. Acousting

microstreaming occurrs when ultrasonic waves propagate through liquids of different viscosity. The molecules of either medium diffuse into the other medium for a short distance near the surface of separation. Besides exerting an alternate pressure with their own frequency, these waves also exert a direct pressure due to radiation which is equal in value to their energy density.[21] The later exerts a steady force against a body immersed in the liquid or at the interfaces between media of different acoustic properties. The phenomenon of cavitation which involves the formation and collapse of microbubbles in the liquid medium propagated by intense ultrasonic waves is responsible for the chemical effects and sono-luminiscence. In what follows ultrasonic radiation pressures on which the direct action theory of image formation is based and cavitation along with its sonoluminiscence on which the secondary action theory of image formation is based are briefly described.

1.31 PRESSURE DISTRIBUTION IN FRONT OF A PISTION SOURCE

A pulsating sphere[21] whose diameter is much smaller than the wavelength of the radiated waves can be considered as a simple source of sound. The magnitude of the volume flow of air at the surface is called the strength of the source. An extended source can be considered as an

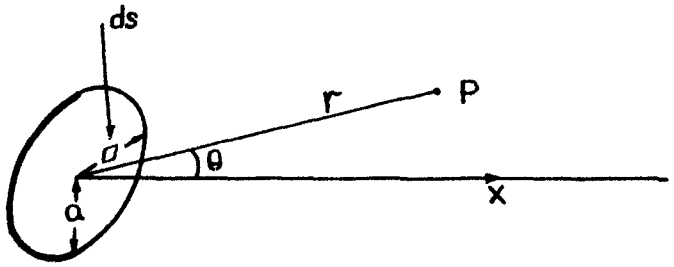


Fig. 1·1A PISTON SOURCE (art 1·3)

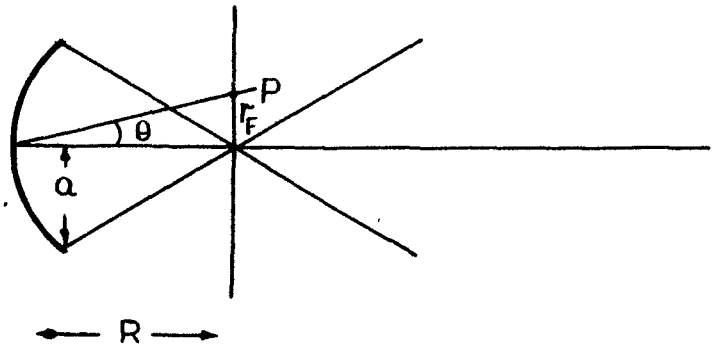


Fig. 1·1B Focussing Bowl (art 3·4)

assemblage of simple sources. Suppose a circular flat topped piston[44] of radius a is set flush in an infinite plane wall and vibrates with a velocity $U = U_0 e^{-2\pi i \nu t}$, where ν is the frequency, U is the velocity at time T and Uo at time t = o, radiating sound in front of the wall. The strength of the simple source corresponding to the element ds is Q = 2 Uods, the effect of the wall being replaced by an immaginary elementary source Uods radiating to the left of the wall. The total pressure at P which is at a distance r from the centre of the piston such that $r \gg a$ due to all the sources making up the piston will be (Fig 1·1A)

$$P = -\pi i \nu \rho U_0 a^2 \frac{e^{ik(r-ct)}}{r} \frac{2J_1(ka\sin\theta)}{ka\sin\theta} \quad \ldots\ldots 1.1$$

where ρ = density of medium

$K = 2\pi\lambda^{-1}$

θ = angle between r and the normal to the piston.

and J_1 = first order Bessel function.

P = o for K a $\sin\theta$ = 3.83, 7.02, 10.15 etc. which indicates that the main lobe will have many side lobes surrounding it. The above expression gives the pressure distribution in a plane at right angles to the beam axis. The corresponding intensity I can be obtained by the equation, peak pressure $P_{max} = (2 \rho C I)^{\frac{1}{2}}$ and the direct pressure[21] by $P_d = \frac{I}{C}$, where C is the velocity of sound in the medium.

Intensity Distribution along the axis

The intensity distribution in front of a circular pistion of radius a, and radiating waves of wavelength λ will be different in the near field, defined by $x < a^2\lambda^{-1}$ and in the far field, $x > a^2\lambda^{-1}$ where X is the distance. In the far field, called the Fraunhoffer region the intensity decreases as X^{-2}. But in the near field called the Fresnel region there will be position of maximum and minimum intensity. The position[22] of the maxima on the beam axis are given by

$$x = \frac{(a/\lambda)^2 - (n-1/2)^2}{(n-1/2)^2\lambda} \quad \text{where } n = 1, 2, 3 \text{ etc.} \quad \ldots\ldots 1.2$$

1.32 ULTRASONIC CAVITATION:

Intense sound waves while propagating through the liquid produce gas filled, vapour filled or empty cavities. The production and subsequent collapse of these cavities and the effects that they induce on the medium or on the surroundings in which they are produced is known as cavitation.[23] Because fluids have low shear strength the only wave type of importance as far as cavitation is concerned is the longitudinal wave which consists of alternate rarefactions and

compression moving along the axis of propagation. In a tank with reflecting walls standing waves are set up, forming nodes and antinodes. If the power input of a travelling wave, or more usually a standing wave in which the reflected energy adds to the transmitted energy, is sufficiently increased the rarefication will stretch the fluid so violently that it may be torn apart. The magnitude of the negative pressure required is given by the expression $p = 2\sigma/R$ where σ is the surface tension of the liquid and R is the radius of the cavity formed. A negative pressure of the order of 10^4 atmospheres is required to form cavities of moleculer dimension in pure water. The tearing apart of the liquid occurs at weak spots. The weak spots in a liquid may be minute dust particles entrapping on themselves tiny gas bubbles, absorbed gas or microbubbles. Nuclii for cavitation[24] also arise due to minute solid particles in the liquid which are not wetted by the liquid, or if they contain cracks or pores such that gas molecules separate the solid and the liquid phases. Cosmic ray particles[25] also provide nuclii. The cavities that are formed are filled with the vapour of the surrounding liquid. Gases dissolved in the liquid also penetrate into the cavities. These cavitation bubbles in certain liquids form the centres which emit light, and this phonomenon is called sonoluminiscence.[26]

G.W.Willard[23] has made a series of high-speed photographs which led him to the conclusion that the intial cavities grow until they reach a size which will oscillate with the applied accoustic oscillations. The size of the bubble at an applied frequency of 1 MC/s is 6 microns. At resonance, the bubbles vibrate violently and collapse, giving rise to shock-waves, enormous pressure differences of the order of 100,000 atmospheres, and temperature rises to about 2700°C. In general, greater the viscosity of the liquid, greater is the ultrasonic intensity required to cause the appearance of cavitation bubbles. The minimum sound intensity[27] for an ultrasonic wave of frequency 15 Kc/s to ~~prince~~ produce cavitation in tap-water is 0.16 watt/cm.^{2} In general, the sound pressure threshold required for cavitation falls with the increase in the temperature of the irradiated liquid. Cavitation occurs relatively easily at a water-glass interface if the glass walls of the vessel are coated with organic substances which make the walls hydrophobic. Cavitation is usually absent in a completely degassed liquid. Polotoskii[13] observed that the yield of hydrogen peroxide, nitrites and nitrates in irradiated acquous solutions was greatly reduced when the air-pressure in the irradiated vessel was 100 mm or 4100 mm Hg. The yield showed a maximum at 1520 mm of Hg.

Ultrasonic waves produce many chemical reactions like liberating iodine from potassium iodide solution and enhance many chemical actions. They also produce luminiscence in some liquids. Though it is now established that these effects accompany cavitation the exact role played by shock waves, enormous pressure and temperature or electrical charges produced in cavitation is not understood. Pinoir and Pouradier[12] and Arkangelskii[16] attributed the blackening of photo-emulsions in the absence of sono-luminiscence to the enhancement of the chemical action of the liquid medium on the emulsion.

1.33 SONO-LUMINISCENCE :

It is a phenomenon in which certain liquids cavitated by intense ultrasonic waves emit light[26] in the visible or near-visible region. This phenomenon was reported by Zimakov[28] and Marinesco[1] when they observed a blackening on a photographic plate exposed to ultrasonics. Liquids like water, ethyl alchohol etc., exhibit[29] sonoluminiscence and liquids like carbon tetrachloride, ethyl ether etc. do not show sonoluminiscience.[30] An addition of a few drops of CCl_4 to water greatly increases[31] the intensity of luminiscience. Degassed water[32] and water saturated with ether, hydrogen etc. shows no luminiscience but water saturated with air,[33]

oxygen etc. shows increased luminiscence. The results on sonoluminiscence are very controversial. According to Chambers,[34] glycerol and nitrobenzol emit intense luminiscence. Laufer and Srinivasan[35] and Negishii[11] have observed glycerol to emit intense sonoluminiscence in the presence of water only. In case of nitrobenzene; though Jarman[29] observed more luminiscence, Laufer and Srinivasan[35] etc. did not detect any luminiscence. The results on the variation of intensity with temperature have also remained contradictory. Chambers[5] observed that in many liquids including water the intensity of luminiscence decreases with increase in temperature but Alfredson[36] observed an intensity maximum around 25°C in water.

Pasunoff[37] observed intense luminiscence in water saturated with oxygen in the wavelength range 4450-5580 A°. In the case of acqueus solutions of luminol[38] the spectrum extends from red to violet region and is also known to have ultraviolet components having maximum intensity around 2300 A°. Gunther[39] et al observed that sonoluminiscent flashes occur at the end of the ultrasonic compression phase and the duration of the flash is less than 10^{-7} Sec. But Jarman[29] observed that the sonoluminiscent flash does not coincide with the collapse of the cavitation bubble and that it occurs within a tenth of a period at the sound pressure minimum. Besides the results on sonoluminiscence intensity being contradictory,

the origin of sonoluminiscence is also not yet clear. There are several theories on its origin and they have been briefly discussed below:

(a) ELECTRICAL MIRCODISCHARGE THEORY

The electrical microdischarge theory proposed by Frenkel[40] postulates that thin non-spherical lens shaped cavities of molecular dimensions are abruptly produced in the cavitated liquid when it tears apart. Great electrical stresses are developed in the cavity and electrical charges of different sign predominate on the opposite walls of the lens. According to Frenkel the electric field strength E, in the bubble is given by the equation, $E = 4er^{-1} Nd$ where d is the distance between the separated layers of the liquid, r is the radius of the cavity, e is the charge of the monovalent ion and N is the number of dissociated molecules in a unit volume. The value of E thus calculated is of the order of 600 volts/cm. If the distance between the walls of the lens is not very great and the vapour pressure in it is low, there will be electronic break-down between the walls of the cavity, giving rise to visible and ultraviolet radiation.

(b) Hot-Spot Theory:

Nottingk and Neppiras[41] investigated the behaviour of a gas bubble in an acoustic field of pressure,

$$P = P_h - P_o \sin wt$$

where P_h is the hydrostatic pressure of the liquid and P_o is the acoustic pressure amplitude. They assumed that during the time preceding the collapse of bubbles, when the accoustic pressure amplitude is small, the gas in the bubble is compressed isothermally, while in the collapse phase, the acoustic pressure amplitude is maximum and the velocity of the bubble walls is very large, the compression is adiabatic. During adabatic compression the rise in temperature is so high that the gas emits black-body radiation. The temperature T, obtained inside the bubble at its minimum radius under adiabatic compression is given by

$$T \simeq T_o \, (P/3Q)^{3(\gamma-1)}$$

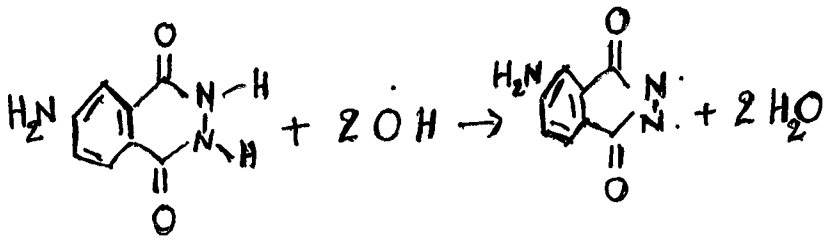
where To is the absolute temperature of the liquid surrounding the bubble, Q is the pressure of the gas in the bubble at its maximum radius and γ is the ratio of the heat capacities of the gas. The value of T thus calculated will be of the order of $10,000^{\circ}K$, and at such high temperatures the gas glows emitting black-body radiation.

(c) CHEMILUMINISCENCE THEORY:

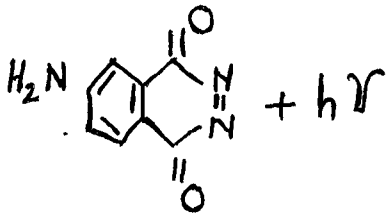
Many workers[42] are of the opinion that sonoluminiscence is closely related with chemical reactions which take place at

the nascent surfaces of the cavities. Free ions are formed when molecules are mechanically or thermally disassociated at nascent surfaces and light is emitted when these ions recombine.

Luminol[38] in an ultrasonic field may be oxidized by OH radicals produced due to the decomposition of water as,



The resulting compound being unstable undergoes reordering by emitting photons as



Jarman[29] has suggested that somoluminiscence can arise from microshocks occurring within the cavities during the final stage of the collapse.

No conclusive evidence in favour of any of these theory is yet available. There is no experimental evidence[32]

to support the formation of lense shaped cavities as assumed in the electrical micro-discharge theory. The chemiluminiscence theory is objected to[35] on the basis that a chemical reaction is not always observed with sonoluminiscence. The validity of the hot-spot theory was questioned by Wagner.[43] He observed that luminiscence occurs within a tenth of a period of the sound pressure minimum and this period is too short for the gas to get sufficiently heated in an adiabatic process so as to emit light.

1.4 THE PROBLEM

As was seen in article 1.1, the blackening of the photographic film by ultrasonics may be due to one or more of the following ultrasonic effects, (1) thermal; (2) hydrodynamic;; (3) mechanical; (4) chemical and optical effects accompanying cavitation. If blackening is due to mechanical action then it will be due to direct action of ultrasonics on silver halide grains of the emulsion, but if blackening is due to other effects then it will be a secondary effect of ultrasonic waves. But till-to-day wether this blackening is a direct effect or a secondery effect has remained controversial.

The direct-action theory has been supported by Marinesco,[1] Reggiani,[1] Trillat,[11] Bennett,[14] Dehn,[4] etc. on the basis of their observations that: (i) Image is formed only in a moist emulsion quite similar to the formation of image by shock-waves only in a moist emulsion by collision excitation. (ii) Better images are obtained at higher temperatures when the emulsion becomes softer. (iii) Image is formed, in certain cases even in the absence of sonoluminiscence.

The secondary action theory of image formation which attributes blackening to sonoluminiscence has been supported by Pinoir,[12] Pouradier,[12] Archangalskii,[16] etc. on the basis of

their observation that: (i) The blackening disappears or is greatly reduced if the intensity of sonoluminiscence decreases for example at low temperatures or when tetrazine is added to water to quench luminiscence, or at very low and at very high pressures. (ii) The density of blackening increases if few drops of CCl_4 are added to water to enhance luminiscence. (iii) Ultrasonic waves enhance the fogging due to the action of developer or water on the photo-emulsions.

The present investigation is an attempt to understand the mechanism of action of ultrasonic waves in causing the blackening of photographic films. Plane and focussing discs-made of peizo-electric ceramics which are recently available have been utilised. A large number of ultrasonographs have been obtained varying such parameters as the intensity of ultrasonics, temperature, speed of the film, immersing liquid etc. Films have been directly exposed to ultrasonic waves from a magnetostrictive oscillator in the absence of a liquid transmitting medium. The quantitative measurements on blackening are made by keeping the films immersed in distilled water which is known to have very little action on the photographic emulsion and varying the above mentioned parameters. The results on intensety of sonoluminiscence at different temperatures and in different

liquids and the wave-length of sound in those liquids have been independently measured. The dependence of the density of blackening on temperature and humidity and the changes in the emulsion on absorbing water have been studied. These results are disscussed and compared with the results that have been reported so far and are used to evolve a suitable mechanism of ultrasonography.

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C H A P T E R II

EXPERIMENTAL

The details of the peizo-electric and magnetostrictive transducers and the construction of an RF Oscillator to excite them have been described in the beginning of this chapter. The measurement of the intensity and wavelength of the waves emitted by them has also been described. This is followed by the description of the assembly of the apparatus to obtain ultrasonographs and sonoluminiscence flux and of the construction of an optical densitometer to measure the blackening of the image. The chapter ends with the experimental details to measure the amount of water absorbed by the film and the effect of temperature and humidity on its blackening.

2.1 PRODUCTION OF ULTRASONIC WAVES.

Ultrasonic waves were produced using peizo-electric and magnetostrictive transducers. A brief description of these transducers is given below.

2.11 PEIZO-ELECTRIC CRYSTALS :

High frequency ultrasonic waves can be produced using peizo-electric transducers which transform electrical oscillations into mechanical oscillations. Peizo-electricity is a property possessed by certain crystals like quartz, tourmmaline, cane - sugar etc., which when subjected to pressure or tension develop electric charges on definite surfaces. Conversely if an electric field is applied along a definite direction called the peizo-electric axis the crystal expands or contracts in certain other directions. Quartz found extensive applications since it is dense, hard, strong, resistant to chemical attack, impervious to moisture and can be easily worked out. But quartz has high impedance and in practice if high power levels are to be obtained, it will be necessary to use radio-frequency potentials of several thousand volts.

A major improvement in the field was the discovery of a new group of crystals known as the ceramic crystals. They are manufactured by heating a mixture of metallic oxides in the furnace and this results in a solid mass

that resembles earthenware. This has poor peizo-electric characteristics as it comes from the furnace but it can be improved upon by the polarisation process. This process consists of keeping the crystal in a powerful electro-static field. Suppose a flat disc is to be polarised, first its opposite faces are silvered to make them conducting. They are then provided with connecting wires and the crystal is kept immersed in oil. The temperature of the oil is raised above the Curie temperature for the material and then a steady voltage of the order of 200 volts for every millimeter thickness of the crystal, is applied. The temperature is then steadily reduced below the Curie point. The disc will now behave like a quartz disc of similar type. This polarisation is reasonably permanent but it rapidly deteriorates as soon as the crystal reaches the Curie point once more. It can however, be repolarised.

(A) Plane crystals : In the present investigation we have used X-cut (longitudinal) crystals with parallel faces and made of lead zirconate ceramic, type PZT -2 and PZT -4 details of which are given in Table 2.1.

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Table 2.1 : Details of the peizo-electric transduvers.

Ceramic	PZT-2	PZT-4
Frequency in MC/s	3	3
Thickness in cm	0.15	0.080
Diameter in cm	2.0	2.0
Curie Temp. ^{o}C	300	325
Manufactured by	National Physical Lab. New Delhi.	Valpey crystal Corpn. Holliston. Mass, U.S.A.

A PZT-2 crystal of frequency 1 Mc/s and thickness, 0.3 cm. was manufactured and the PZT-4 crystals were chrome plated by sputtering was the N.P.L. New Delhi. These crystals were mounted in a holder made in our work-shop. Holders with solid metal backing were used in the investigation. The crystal was hemmed between a metal ring of diameter, 1.4 cm. and a backing-plate and both of them were separately connected to the output terminals of the oscillator.

(B) Focussing Bowl : Ultrasonic waves of large intensity were required to study sonoluminiscence and for this purpose a ceramic crystal which was spherical in shape was used as it could focus the ultrasonic waves to produce intense waves at its centre of curvature. The details about this crystal are in Table 2.2.

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Table 2.2 : Details of the focussing crystal.

Ceramic	$Ba\ TiO_3$
Internal diameter	11.62 cm.
Internal aperture	9.06 cm.
Thickness	0.62 cm.
Internal height	2.18 cm.
Density	5.5 gm/cm3
Frequency	450 kC/s
Curie temperature	120° C

This crystal was manufactured by the Brush Clevite Corporation, Clevland, U.S.A. It had two fired in leads on either side of it and could be readily used by connecting these leads to the output terminals of the oscillator.

2.12 MAGNETOSTRICTIVE TRANSDUCER.

If the intensity of the ultrasonic waves is large then it is possible to expose photographic films to ultrasonics without any liquid transmitting medium. Since the attenuation of the ultrasonic waves is proportional to the square of the frequency, low frequency waves obtained by a magnetostrictive oscillator were used.

The magnetostrictive effect[2] occurs in ferromagnetic materials such as iron, nickel, cobalt and certain special alloys. When these materials are subjected to magnetic fields there will be a change in their physical dimensions. Similarly there will be a change in their magnetic properties if their dimensions are altered by external force. The magnetostrictive effect which involves the change in the length of the material along the direction of the magnetic field is called Joule effect and is utilised in the generation of ultrasonic waves.

Magnetostriction can be explained by consideration of the domain theory. In an atomic system the orbital electron produces a magnetic moment. Due to random orientation of atoms in a solid, the magnetic moments of separate atomic groups are generally cancelled out. However ferromagnetic materials are an exception to this. In thiese systems an exchange force exists that causes all the atomic magnetic fields within a volume of about 10^{-8} cm^3 to lie parallel to each other. These domains of magnetic moments can be aligned by an external magnetic field applied along one of the many fixed directions called the directions of easy magnetisation which depend on the structure of the crystal.

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When the external magnetic field is increased the domains originally magnetised in the direction of the field grow in size taking over the other differently oriented domains until the complete crystal becomes a large domain. As the field becomes more intense the domain in each crystal rotates until it is parallel to the field and in doing so the material expands or contracts externally.

By passing electric current through a solenoid, a suitable magnetic field can be generated along its axis. A sine wave source that excites the solenoid will produce directional changes in the core at twice the exciting frequency. If a varying external magnetic field is produced by a solenoid whose core is formed by the magnetostrictive element, it will operate in two directions of easy magnetisations which are opposite to one another. Since the initial system consists of completely random domains their average movement will cancel out. But if an initial magnetisation is given to the core and it is then subjected to a varying magnetic field the domain movement will be considerably greater in one direction. This causes a change in length of the order of 10^{-6} cm per cm. Whereas iron expands in a weak field and contracts in a strong field, nickel contracts at all field strengths. All magnetostrictive

materials are temperature sensitive and the material loses its magnetostriction as the temperature rises until the Curie point is reached where all magnetic properties cease.

In the present investigation a magnetostrictive oscillator containing a nickel transducer of frequency 20 KC and manufactured by Dr. Lehfeldt and Co., Heppenheim, Germany was used . The length of the transducer, d = 7 cm and it possessed a node at the centre of its fundamental mode of vibration. It was fitted with a tapering coupling stub of length 3d cm.

2.2 INTENSITY, WAVELENGTH AND FREQUENCY OF ULTRASONIC WAVES:

Intensity : It is customary to express the intensity of the ultrasonic waves as the ratio of the total power output by the crystal to the effective area of the crystal. The effective area can be easily measured and the total power output is obtained by the calorimetric method using the following formulae. If waves are passed through a liquid for a known time t, the total power output $W = JH$ and $H = (m_1 s_1 + m_2 s_2) (\theta_2 - \theta_1) t^{-1}$, ... (2.1)

where J is the mechanical equivalent of heat θ_2 and θ_1 are the initial and final temperatures, m_1, m_2 and s_1, s_2 are the masses and specific heats of the liquid and calorimeter respectively.

In the near field or the Fresnel region, there will be positions of intensity maxima and minima on the beam axis (art. 1.31) and it is necessary to know the wavelength of sound in the liquid medium in order to calculate these positions.

Wavelength : The wavelength of sound λ_s in the liquid medium was measured using Debye and Sears technique. The experimental arrangement[3] is shown in Fig. 2.1. The whole assembly of the apparatus was built by Andhra Scientific Co. India. The Ultrasonic waves passing through a liquid are elastic waves in which compression and rarefaction travel one behind the other at regular distances apart. The density of the liquid is therefore changing periodically in the direction of the sound wave and hence also its index of refraction. This variation in refractive index is used to produce diffraction of light. This diffraction pattern is visible on a ground glass plate and is measured using a travelling microscope. λ_s is calculated from the formula

$$\lambda_s \sin \theta_k = k\lambda_l \qquad \ldots\ldots\ldots (2.2)$$

① LIGHT SOURCE

② LIQUID

③ QUARTZ CRYSTAL

④ SCREEN OF MICROSCOPE

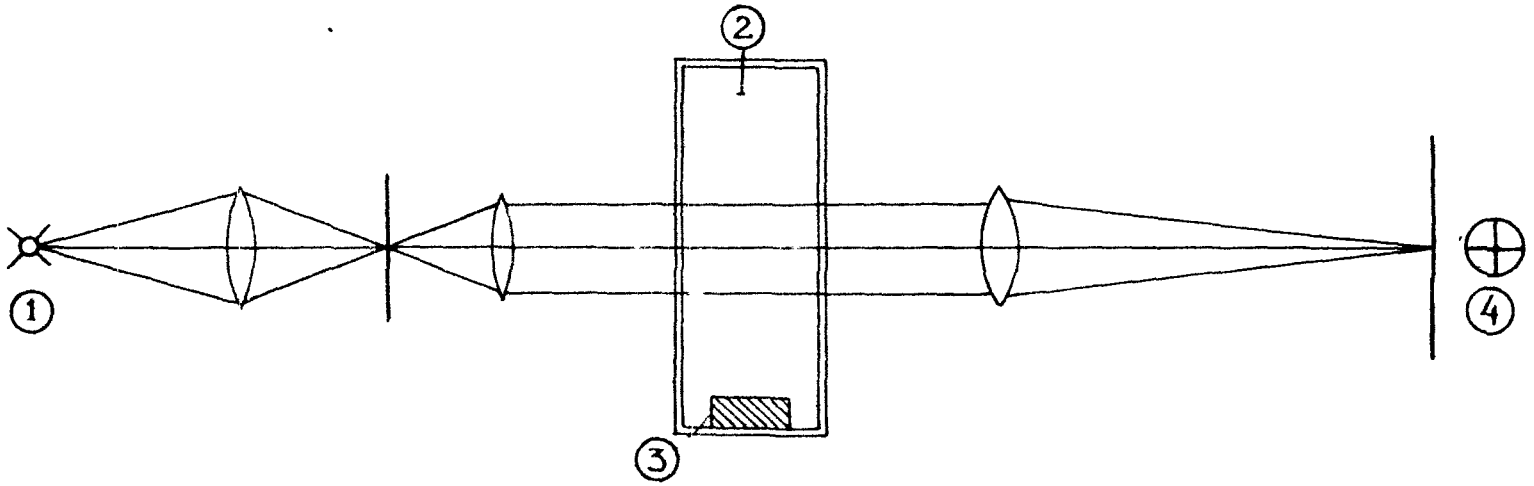

Fig. 2.1 DIFFRACTION OF LIGHT BY ULTRASONICS

where θ_k is the angle of diffraction for the k^{th} order and λ_l is wavelength of the monochramatic light. Since A, the distance between the screen and the diffraction greting set up by ultrasonics is very large as compared to d_k, the distance of the k^{th} diffraction image from the central image, sin θ_k can be replaced by d_k/A . A sodium vapour lamp was used to produce monochromatic light of $\lambda_l = 5896A^{o}$. Ultrasonic waves were produced by a quartz crystal of frequency, n = 3.2 Mc. The velocity of sound in the liquid V, can be readily obtained from the formula, $V = n \lambda_s$.

Frequency : The frequency of the crystal was quoted by the manufacturers. The crystal can vibrate in its fundamental or odd harmonic modes. The intensity of the waves of harmonic modes is very small and so the crystal was used to emit waves in its fundamental mode and its value was checked by connecting the oscillator to an oscilloscope.

2.3 RF Oscillator : The peizo-electric crystal was excited by an RF Oscillator of output power 100 watts and frequency range 1 to 5 MC/S. The DC voltage to the Oscillator was supplied by a stabilised power supply, operating in the range 0-500 Volts and 0-500 milliamperes,

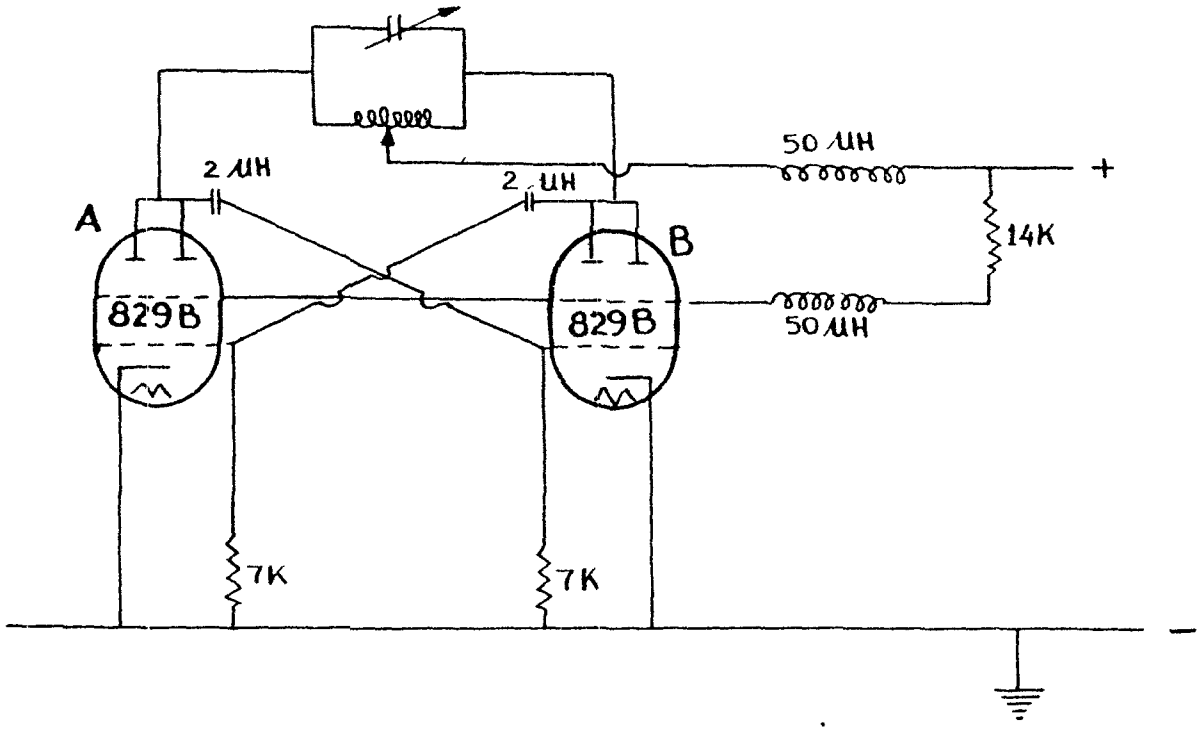

Fig. 2·2 R.F. OSCILLATOR

built by the General Electrics Company, U.S.A. The oscillator was constructed in this laboratory. Its circuit diagram is given in Fig. 2.2 and its working is briefly described below.

An oscillator can sustain oscillations and will be useful in practice if the output power is sufficient to overcome the losses of the circuit and also to provide the power that is transferred to the external circuit. This can happen if the tube acts as a negative resistance.

The oscillator[4] that has been constructed is essentially a plate coupled multi-vibrator oscillator withan L-C tank circuit connected between the plates of the two 829B tubes. It acts as a negative resistance oscillator. The two tubes have identical characteristics and if the voltage between the two points A and B is zero there is no flow of current between them. But if a small increment of voltage is applied between A and B, a small current will flow between them. This current will increase the plate voltage and decrease the grid voltage of one tube and decrease the plate voltage and increase the grid voltage of the other tube. If the resulting amplification is large then the change in the plate current exceeds the

current flowing between A and B and will be in a direction opposite to that of the applied voltage. So apparently a negative resistance will be produced between A and B. If an LC tank circuit is tuned between A and B, sustained oscillations can be obtained. Though the multivibrator by itself is a class C oscillator since there is only instantaneous flow of current the addition of the tank circuit makes it a class A oscillator because then the current will flow in the plate circuit throughout the cycle.

The two RF chokes of 50 μH each, stop the AC component from getting back into the power supply. The two condensers of 2 μH each cut off the DC components and feed back RF Voltage of proper phase to the grids. The 14 K resistance keeps the screen grid at a slightly lower potential than the plate. The 7KΩ resistances act as grid bias resistors and supply proper voltage to the grids. The frequency of the oscillator $f = 1/2\pi\sqrt{LC}$ where L is the inductance of the coil and C is the capacitance. Induction coils were wound using the formula[5]

$$L = 0.2a^2n^2 / 3a + 9b + 10c$$

where a = 2.5", the diameter of the coil; b = 1.6", the distance between the extreme turns of the coil, c = 0.4",

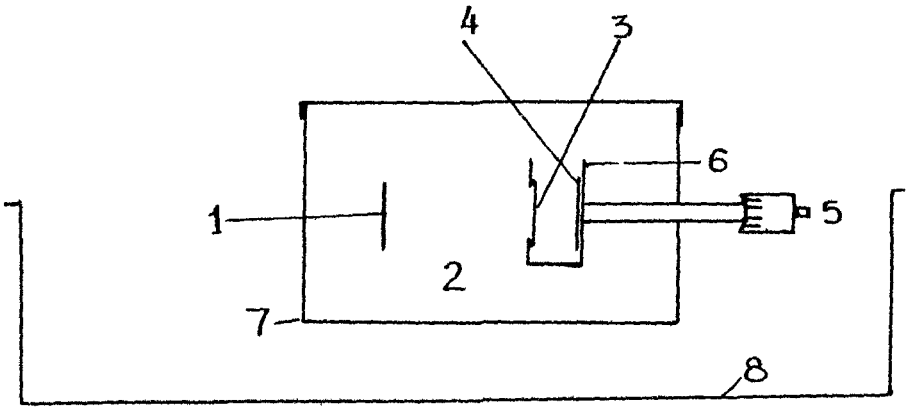

FIG 2.3 Experimental Arrangement to obtain Ultrasonographs (1) Transducer (2) Transmitting liquid (3) Window (4) Photo-film (6) Micrometer screw (6) Cell containing test liquid (7) Light proof box (8) Cooling tank.

the diameter of the wire and n = 16, the number of turns of the coil. The value of L thus calculated was about 15 μH and using a ganged condenser in the range 0-300pf oscillations in the frequency range 2.5 MC/S to 5MC/S could be obtained. Another coil with n = 50, was used to obtain oscillations in the frequency range 0.8 to 2.5 MC/S

The piezo-electric crystal was excited by connecting it across a secondary coil would round the above inductance coil. One surface of the crystal was earthed. The RF voltage across the crystal in the range 50 to 110 volts was measured using a Philips vaccum tube voltmeter.

2.4 Assembly to obtain Ultrasonographs :

2.4 (A) Peizo-electric Oscillations : The assembly of the apparatus is shown in Fig. 2.3 and 2.4. The ultrasconic waves from the Peizo-electric crystal were transmitted through transformer oil to a stainless-steel cell. This cell was 2 X 4 X 5 cm. in size and had a 2 X 2 cm. removable window of polythene sheet of thickness 5 microns. Stainless-steel does not react with the test liquid. The incident ultrasonic waves that were transmitted through the window propagated through the test liquid to irradiate the photographic film kept in the cell. The position of the cell could be accurately adjusted by a micrometer, and a gear

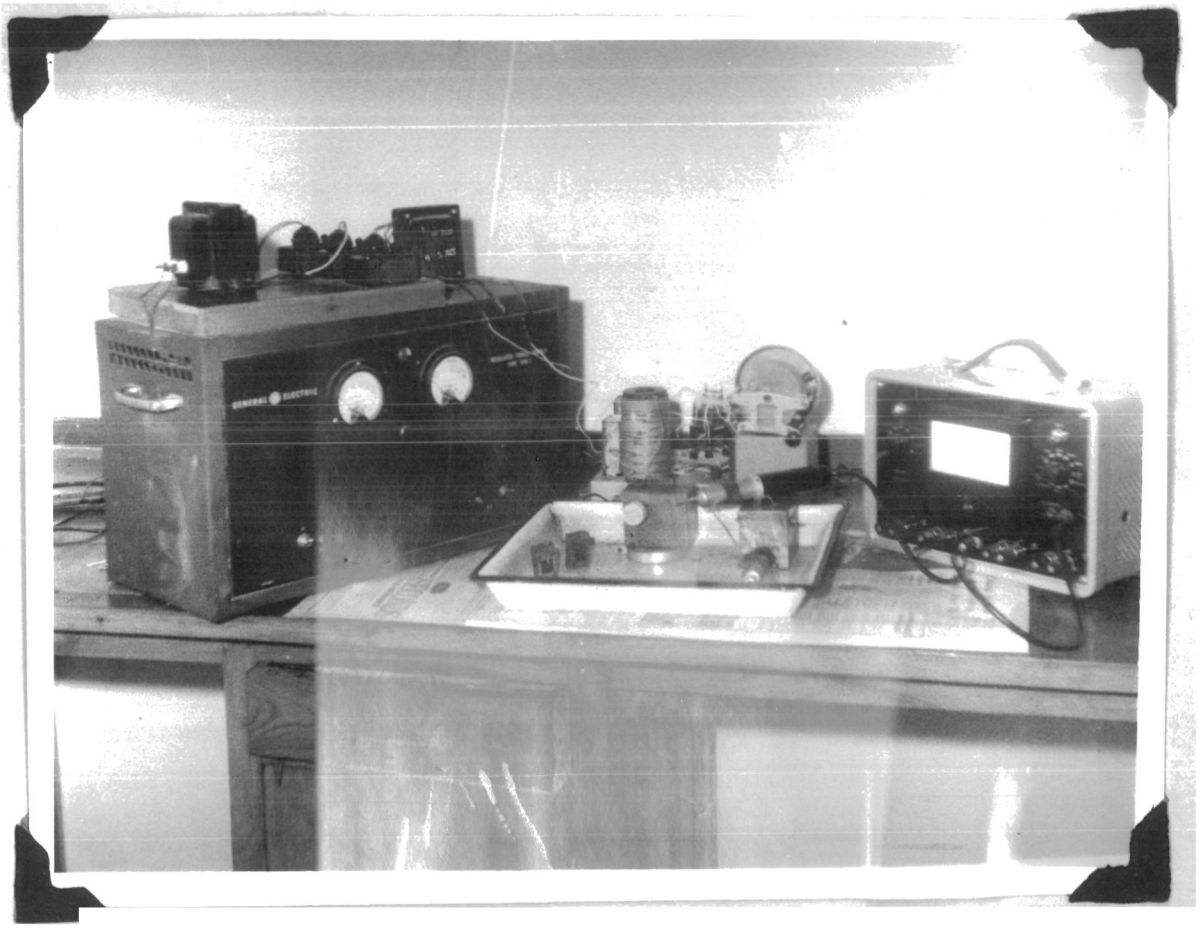

FIG 2.4 Assembly to obtain Ultrasonographs.

arrangement enabled to keep the cell at different angles. The film was cut from a film-roll obtained from the local market, and its entire exposure and processing was done in total darkness. The peizo-electric crystal, the transmitting liquid and the test-cell were all kept in a 6X6X8 cm. copper-box with a removable lid. The box was light-proof when the lid was closed. This copper-box was kept in a big tray containing water which helped to control the temperature of the liquid inside the container and the cell. The temperature of the water in the tray was adjusted by adding ice, and was about 5° C less than the temperature of the liquid inside the test-cell. The temperature of the test-liquid was measured before and after the exposure and it changed by about 2° C during the exposure. The film was then removed and developed.

2.4 (B) MAGNETOSTRICTIVE OSCILLATION :

The assembly of the apparatus to expose photographic films to ultrosonic waves obtained from a magnetostrictive oscillator is shown in Fig. 2.6. Electric oscillations of frequency 20 KC/S were obtained from an oscillator of frequency range 30 cycles/S-30 KC/S built by Bharat Electronics, Bangalore. The out-put voltage of the oscillator was increased to 120 Volts by means of an amplifier manufactured

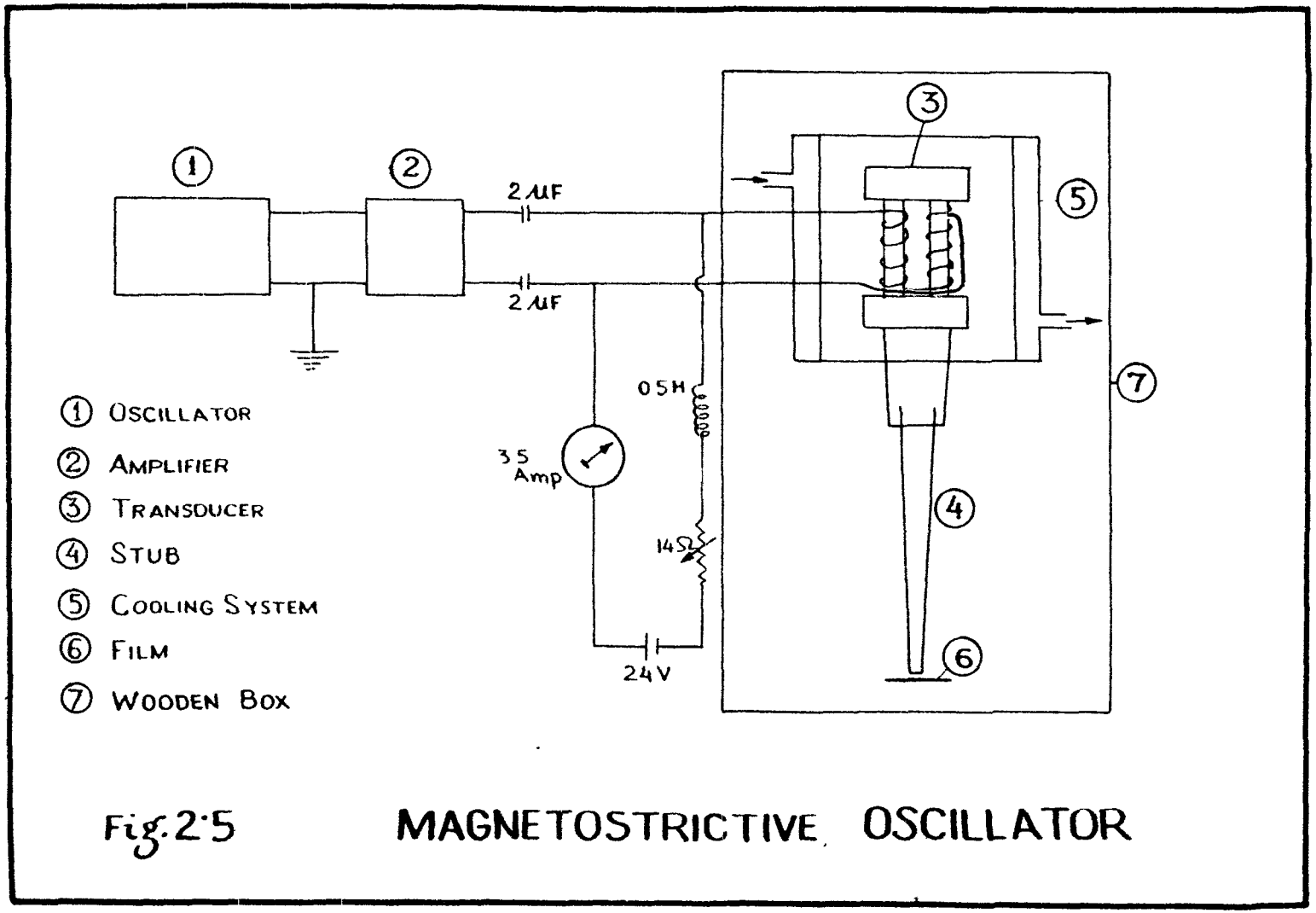

Fig. 2·5 MAGNETOSTRICTIVE OSCILLATOR

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by Motwane Private Ltd., Bombay. This oscillatory current was fed to the solenoid of the magnetostrictive nickel transducer. The prepolarising current of 3.6 amperes and 24 volts, obtained by a battery was also fed to the solenoid. The 2 μF condensers stopped any direct current voltage from entering the alternating current supply and the 0.6H induction coil stopped any alternating current voltage from entering the battery circuit. The oscillations produced were coupled to air by a connecting tapering stub. The entire transducer assembly was enclosed in a light proof wooden box. The rise in temperature of the transducer was checked by the continuous flow of water in the double walled vessel surrounding it. The photographic film was exposed to ultrasonic waves by keeping it in air directly in front of the coupling stub at a distance of about 2-3 millimeters.

2.6 BLACKENING OF THE FILM :

The latent image was visible on development and fixing of the film. The amount of blackening of the image was a measure of the interaction between ultrasonics and the emulsion.

A. Development : The exposed film was developed in D-19 developer for 4 minutes in total darkness. The chemical composition[6] of this developer is given below:

D - 19 Developer

Water	1000 CC
Metol	2 gm
Sodium Sulphite	90 gm
Hydroquinine	8 gm
Sodium bicarbonate	52.5 gm
Potassium Bromide	5 gm.

B. Fixing : After development the film was dipped in water for half a minute and put in the fixer for five minutes. The fixer consisted of a saturated solution of sodium thiosulphite (hypo) in water. The film was carefully washed in water and allowed to dry in the air.

C. Density : The amount of blackening of the photographic film is measured in terms of density[7] which was defined by Hurter and Driffield as the mass of silver per unit area. They observed that the mass of silver in the image is directly proportional to the absorption of light i.e. to its optical density. If I_t and I_o be the intensity of light incident on the sample and transmitted by the sample respectively then its optical density is defined as $\log I_o/I_t$.

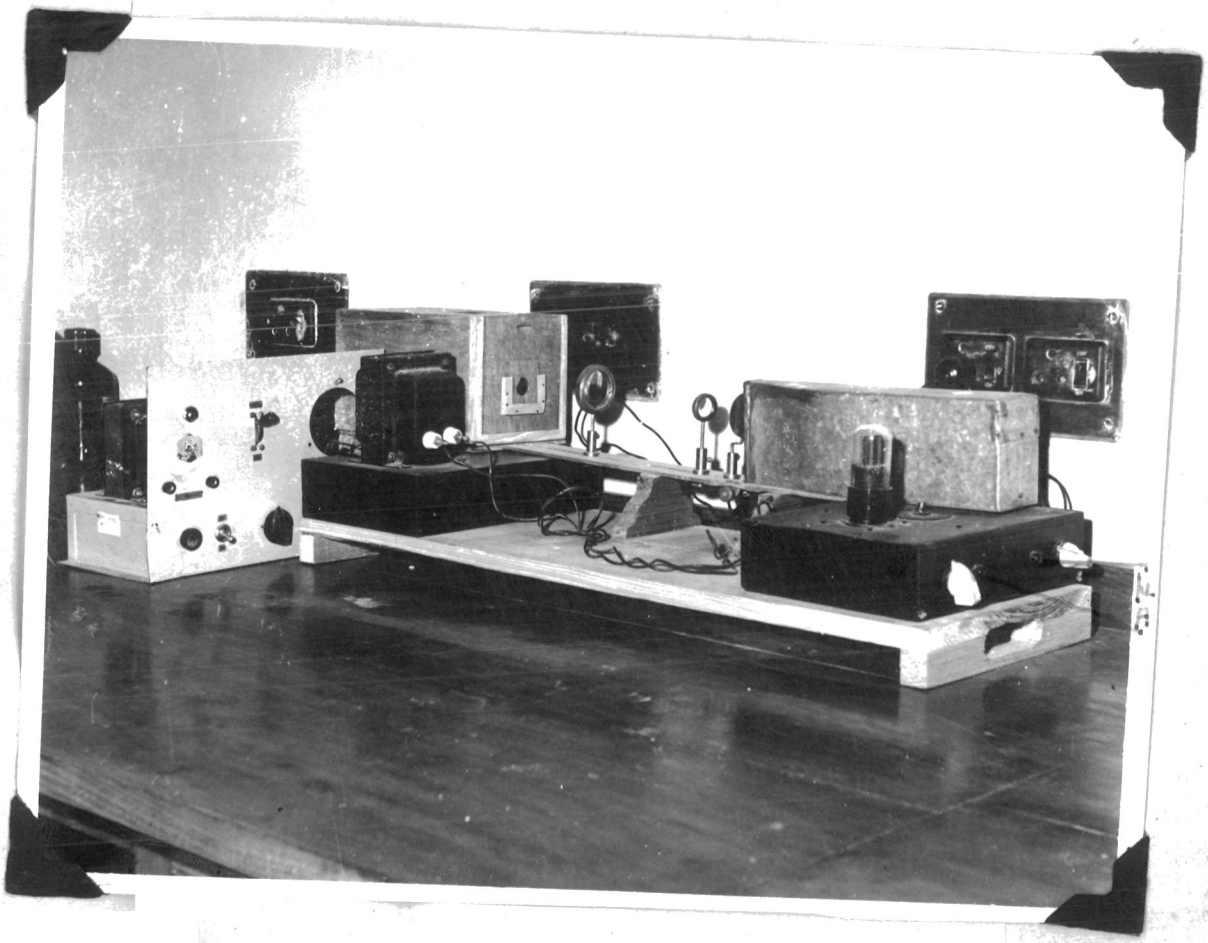

FIG 2.6 Optical Densitometer.

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In practice the density invariably refers to optical density and is the logarithm of the ratio of the light intensity measurements by a photometer without and with the blackened film. The instrument used to measure the density of blackening is called a densitometer.

2.6 DENSITOMETER :

The details of the densitometer constructed in this laboratory are shown in fig 2.6 and 2.7. An ordinary bulb of 200 watts operated at 230 volts and enclosed in a wooden-box having a small circular aperture in its front served as the source of intense light. The beam coming out from the aperture was converged by a system of lenses and an intense narrow beam of light fell on a slit. The slit had a circular opening of diameter less than a millimeter and the film whose density of blackening was to be measured was kept on the other side of the slit in immediate contact. The position of the film could be easily adjusted such that light could scan the full image on the film. The transmitted light liberated electrons from the cathode of the photocell RCA 923 to produce electric current of about 10 microamperes.

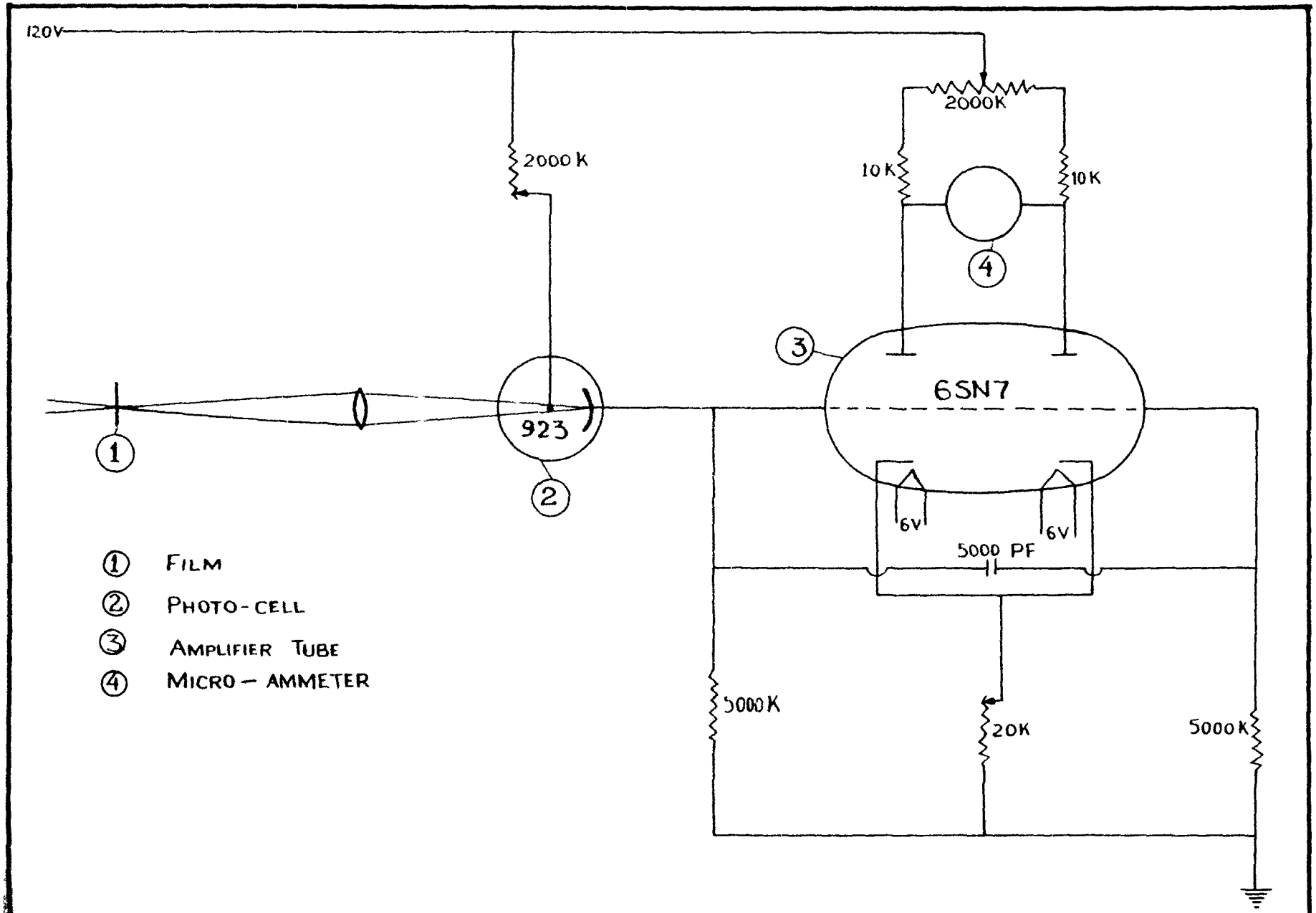

Fig. 2·7

DENSITOMETER

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The current from the photocell was amplified by a 6SN7 double triode which acts as a differential amplifier as shown in Fig. 2.7. It was operated at 100 volts. The 5000 PF condenser allows the D.C. output from the photocell to be fed to the grid of only one tube and A.C. output if any, to the grids of both the tubes. The 500 KΩ resistances act as grid bias resistors. The variable 20 KΩ resistance acts as a cathode bias resistor and the variable 2000KΩ and fixed 10 KΩ resistances were used to adjust the potential difference so as to obtain zero current in the microammeter. The difference in current across the plates of the two tubes was read on a microammeter in the range 0 to 250μ A. The current thus measured was taken to be proportional to the intensity of light falling on the photocell. Deflections in the microammeter were noted when the narrow beam of light was made to pass through different regions of the film.

2.7. Assembly to study Sonoluminiscence :

Sonoluminiscence is the light emitted by liquids cavitated by ultrasound. Its intensity will depend on the intensity of ultrasonics, nature of the liquid, temperature of the liquid, etc. But its origin is not clearly understood and the results on its intensity

measurements are contradictory. So its intensity at different temperatures and in different liquids have been independently measured. The experimental arrangement is shown in Fig. 2.8, and its details are given below.

The ceramic bowl shapedd crystal (2.1 B) of frequency 460 Kc/s was used to obtain intense ultrasonic waves to study sonoluminiscence. The crystal when excited byan RF oscillator, focussed the waves at its centre of curvature. " Ultrasonic Generator" model B-600, manufactured by Peizo-Products company, Framingham, Mass, was used to excite the crystal . The oscillator had a frequency range of 120 Kc/s to 1 Mc/s with an input power in the voltage range of 0-1500 and current range 0-200 milliamperes. The RF voltage across the crystal in the range 0 to 30 volts was measured by a Hewlett Packard Vacuum tube voltmeter. The ultrasonic waves were transmitted through water and then through a thin polythene window to 30.c. of test-liquid contained in a glass beaker. The top surface of the liquid was just above the centre of curvature of the ceramic bowl. The sonoluminiscence produced in the liquid was guided by a perspex rectangular block 10 X 4 X 3 cm in volume to a photomultiplier tube, RCA 931 A, kept enclosed in a metallic box with a 3 X 2 cm. opening. This tube was operated by electric power, 1250 volts and one milliampere current, supplied by a High voltage Unit

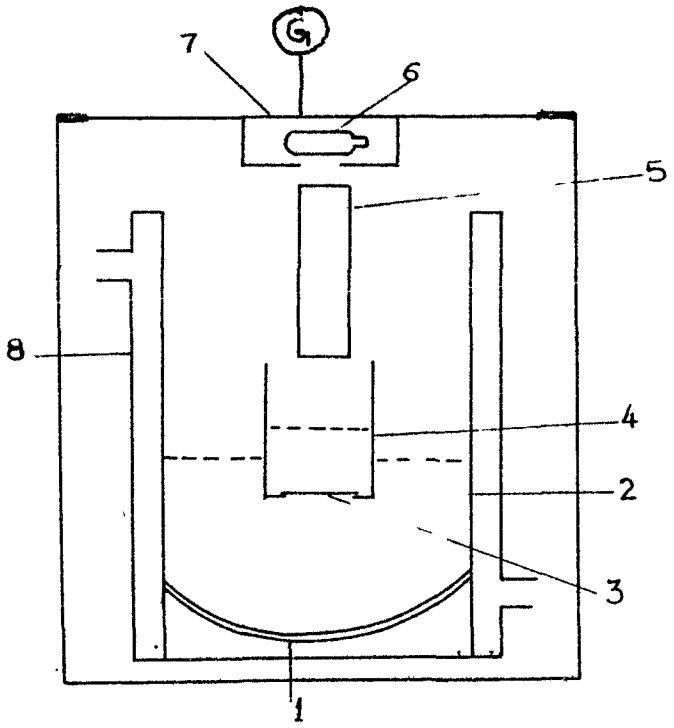

FIG 2.8 Experimental Arrangement to Measure Foncluminiscence Flux (1) Curved transucer (2) Transmitting liquid (3) Window (4) Beaker containing test liquid (5) Light-guide (6) Photo-multiplier tube (7) Wooden box (8) Cooling system.

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HV66 constructed by Atomic Energy Establishment, Bombay. The whole assembly was enclosed in a light-proof wooden-box On passage of ultrasonic waves the temperature of the temperature of the test liquid rose rapidly. The rise in temperature was controlled by circulating water in a double walled outer vessel. The current produced by the pho-multiplier tube was read on a spot galvanometer, manufactured by Cambridge Instrument Co., Ltd., England. The sensitivity of the galvanometer was determined experimentally and was 6×10^{-8} amperes per millimeter. The anode dark current of the galvanometer was 0.16×10^{-6} amperes. Deflections in the range 0-100 mm. were read on the galvanometer for different applied voltages in the range 0-30 across the crystal. It took less than a minute for each set of readings and the temperature of the test liquid changed by about 1^{o} C during this interval.

By removing the perspex guide and keeping a photographic film in the test-beaker, the above set-up can also be used to expose photographic films immersed in different liquids to intense ultrasonic waves.

2.8 APPARATUS TO STUDY THE EFFECT OF MOISTURE AND TEMPERATURE ON THE FILM :

In order to study the variation of the density of blackening due to ultrasonic irradiation on a moist emulsion

with temperature, distance, nature of the liquid, intensity of sonoluminiscence, etc., it will be useful to know the effect of these parameters on the photo-film in the absence of ultrasonic irradiation. The experimental details to study the same are given below :

Change in Weight : When the photographic film was immersed in water it absorbs water. The amount of water absorbed depends on the temperature of the water and on time during which it was immersed. With increase in time of immersion the film absorbs more and more water and gets saturated in about one minute. Small strips of films were cut and immersed in water for different interval of time in the range 5-60 seconds and at different temperatures, in the range 10-35° C. On removing them from the water bath they were quickly dried by filter papers and carefully weighed in a chemical balance correct to 10^{-4} gm.

Change in Volume : Besides a change in the weight of it the emulsion on immersing in water there was a change in its volume too. On absorbing water the thickness of the emulsion increased and practically there was no change in its lateral dimensions. The change in thickness was measured correct to a micron by means of a Cooke's Research microscope fitted with an eye-piece of magnification 10.

Change in Density of Blackening : The density of blackening changes with the temperature of the exposure, humidity of the ambient atmosphere, distance between the source and the film, time of exposure etc. Faint light sources such as (A) Zero-watt bulb; (B) Sodium Iodide crystals with traces of Thallium in it supplied by Harshaw Chemicals, Cleveland, Ohio and irradiated by γ- rays from Ra^{8} source were used. The light source was replaced by α- ray source, Pu-137 while studying the effect of temperature on the blackening. The change in humidity, in the range 0 to 100 %, of the ambient atmosphere, was brought about by keeping the film in a polythene bag containing chemicals like silica gel, copper sulphate, etc.

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C H A P T E R III

RESULTS

Some preliminary results on 1) the effect of temperature and humidity on the blackening of the photographic film; 2) change in weight and volume of the emulsion on absorbing water; 3) measurements of intensity and wave-length of ultrasonics and 4) the technique of ultrasonography etc. are given in the beginning of this chapter. This is followed by the results on ultrasonographs obtained varying such parameters as transmitting and moistening media, intensity of ultrasonics, temperature of the emulsion and speed of the film. Measurement of sonoluminiscence fluxes in different liquids and at different temperatures are also recorded in this chapter. All the above results have been compared with those available in literature.

3.1 PRELIMINARY RESULTS

This Article contains the results of some preliminary work on the (1) blackening of the photographic film; (2) absorption of water by the photographic film; (3) wavelength and intensity of ultrasonic waves, and on (4) techniques of ultrasonography:

3.11 BLACKENING OF THE PHOTOGRAPHIC FILM

It will be useful to know the density range in which density can be taken as a measure of the exposure. Further to disscuss the variation of the density of ultrasonographs with such factors as temperature, immersion liquid etc. it will be useful to know the effect of these parameters on the blackening of the film in the absence of ultrasonic irradiation. These results are given below:

(A) DENSITY-EXPOSURE RELATION

The region in which the density Vs. logarithm of exposure graph is linear depends on the nature of the emulsion and on the development time. ORWO films of speed 120 ASA were immersed in water and exposed to faint light from a zero-watt bulb which was kept at a distance of 150 cm. in a wooden-box having a small aperture. The density values for 4 minutes development are recorded in Table 3.1.

Table 3.1 : DENSITY FOR DIFFERENT EXPOSURE TIME

Exposure time in min.	Density of Blackening
1	0.06
3	0.08
7	0.10
10	0.15
15	0.30
25	0.48
35	0.60
45	0.68
60	0.82

These readings when plotted indicate that densities less than about 0.10 are not a good measure of the exposure. The graph is linear for density values greater than 0.15.

(B) EFFECT OF HUMIDITY

Films were exposed to a scintillating crystal (Art. 2.7) in air, having different relative humidity. The crystal together with the film was exposed to γ -rays such that the doserate was 0.075 mr/hr and the total dose was 5 mr. The crystal was kept inside a polythene bag containing chemical reagents which controlled the humidity. The results are given in Table 3.2.

Table 3.2 : DENSITY AT DIFFERENT HUMIDITIES OF THE AMBIENT ATMOSPHERE

Chemical	Relative humdity %	Density
Silica-gel	0-20	0.85
$CaCl_2$ $6H_2O$	40-55	0.59
Ambient	70	0.48
$CuSo_4$ $5H_2O$	90	0.45

The decrease in the density with increasing humidity is due to latent image fading.[2] Latent image fading is due to chemical processes initiated by the surrounding atmosphere. This has been proved[3] by its study in vaccum. Latent image fading is enhanced at a higher relative humidity of ambient atmosphere.

Shepard and Graham[4] studied sensitivity of the emulsion with its water content. They observed that as the water content is increased the sensivity at first increases; then it passes through a maximum (in the region of 12 to 16%) and subsequently as more water is absorbed the sensitivity decreases.

(C) EFFECT OF TEMPERATURE

Films enclosed in an oven or a refreigirator were exposed to α -radiation from the Pu-239 source for 48 hours.

at a temperature of 3°C, 23°C and 45°C. The corresponding density values[5] are 0.37, 0.38 and 0.37 respectively. This indicates that the film response to temperature variation in dry air is temperature independent in the range 3°C to 45°C.

Temperature changes can effect the movement of the interstitial ions and dis-integration of the pre-latent image speck. According to the Gurney-Mott theory (Art.1.2) a trapped electron must be neutralised by the movement of an interestitual silver ion to that spot. An increase in the temperature will increase the rate of arrival of the interestitial silver ions and hence will increase the sensitivity. Increase in temperature can also increase the thermal disintegration of the pre-latent image speck involving the ejection of an electron from the initial silver atom. But the above results show that a change in temperature of about 40°C does not produce any apparent change in density.

3.12 : MOIST EMULSION

It was observed that the amount of water absorbed by the emulsion depends on the temperature of the water and on the time interval for which it was moistened. The details of these measurements are given below.

(A) CHANGE IN WEIGHT

If a film is immersed in water its emulsion rapidly absorbs water. The weight of the film on absorbing water for three minutes at different temperatures is recorded in Table 3.3. However, this weight includes the weight of a thin layer of water on the surface of the emulsion as it could not be completely removed lest water inside the emulsion was also removed.

Table 3.3 : WEIGHT OF THE MOIST EMULSION AT DIFFERENT TEMPERATURES

Size of the film	6.2 X 2.1 cm
Weight when dry	0.205 gm
Weight of the film backing	0.165 gm
Weight of the emulsion	0.040 gm

Temp. in ^{o}C	Water absorbed in gm.
15	0.060
20	0.066
26	0.076
30	0.094
32	0.102
34	0.114

But 0.04 gm emulsion absorbes only 0.048 gm water at $26^{o}C$ if it is immersed in water only for six seconds. The

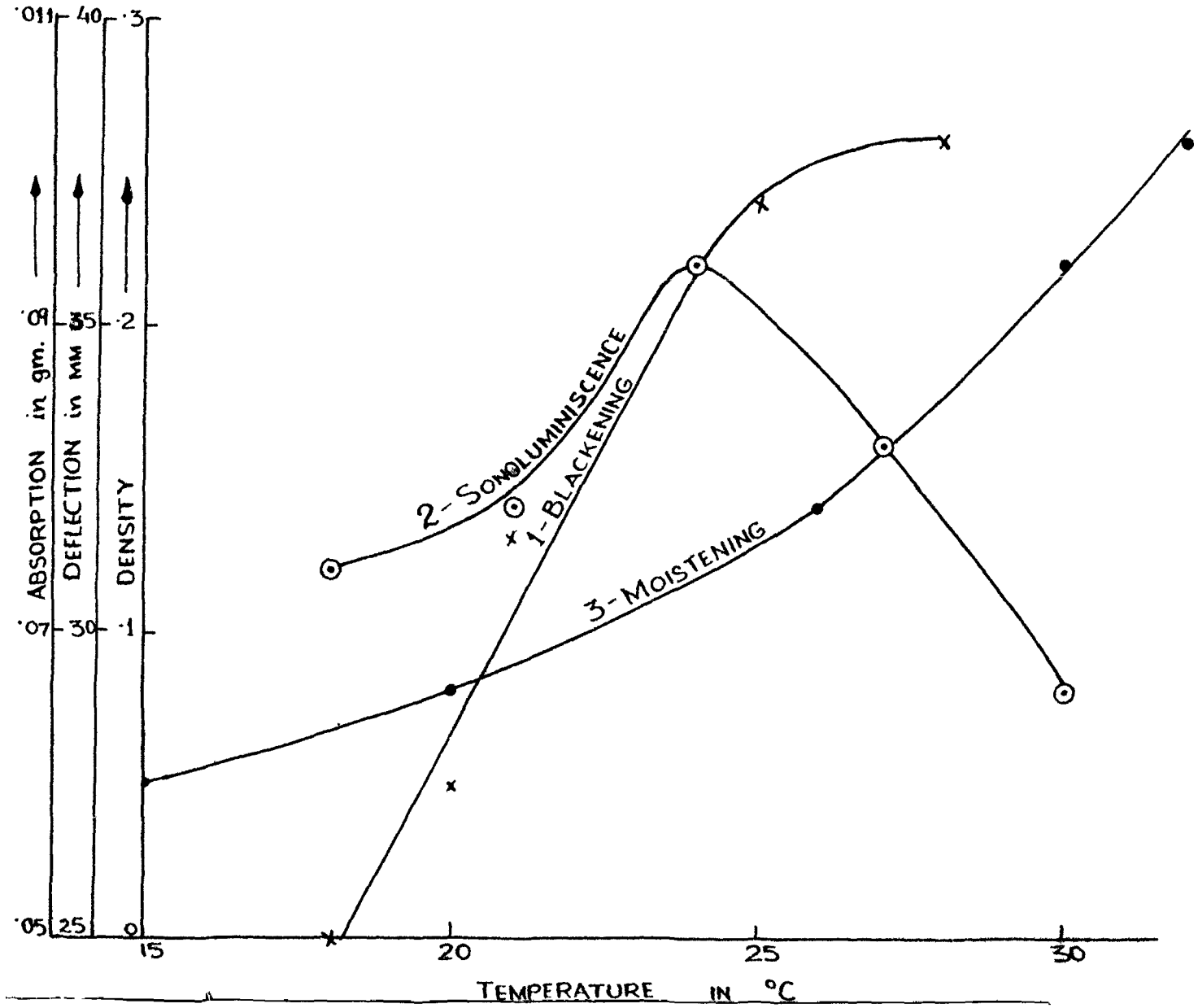

FIG 3.1 Dependence on Temperature of (1) Optical density of the image (2) Sonoluminiscence flux in water (3) Water absorbed by the emulsion.

emulsion scarcely absorbs transformer oil, Xylene, CCl_4, glycerine, nitrobenzene, butyl alchohal or iso-amyl alchohol.

The readings are plotted in Fig. 3.1 and the graph shows that the emulsion absorbes increasing amount of water as temperature increases. However if the film is immersed in water and be irradiated by ultrasonics for about 15 minutes at temperatures of more than $30^{\circ}C$, the emulsion seperates from the backing and no image is formed. The rise in temperature of the emulsion due to absorption of ultrasonic energy, ultrasonic radiation pressure and cavitational effects all help to separate the moist emulsion from its backing. Ordinarily dry gelatin forms a solution in water at $40^{\circ}C$.

(B) CHANGE IN THICKNESS

The thickness of the emulsion layer of the film on absorbing water at different temperatures for three minutes is recorded in Table 3.4. The expansion of the emulsion in the lateral direction was negligible.

Table 3.4 : THICKNESS OF THE EMULSION LAYER

Microscope Setting	Temp.	Microscope readings in microns.
1. Focussed on the surface of the dry emulsion	26°C	15
2. Focussed on the surface of moist emulsion.	14°C	17
3. - Do -	26°C	18
4. Focussed on the film backing without emulsion.	26°C	9

These readings show that that thickness of the emulsion layer on the film is 5.7 μ and it swells to 7.7μ on absorbing water at 14°C and to 8μ at 26°C. So, most of the water absorbed by the emulsion in the temperature range 14 - 26°C is stored inside the porous gelatin and the increase in its volume practically remains the same.

3.13 WAVELENGTH MEASUREMENTS

The wavelength of sound λ_s in different transmitting liquids, was measured in order to calculate (1) the Fresnal and the Fraunhoffer region in front of the plane peizo-

electric crystals (2) the positions of intensity maxima and minima in the Fresnal region; (3) the intensity of the ultrasonic waves in the focal region of the spherical bowl (4) the distance between the nodes at which sonoluminiscence is more pronounced etc. λ_s was calculated using the formula 2.2, $\lambda_s = \frac{KA\lambda_L}{d}$. Usually, distances between 4 to 6 fringes were measured and the average distance between two fringes was determined. The values of d, λ_s and velocity of sound $V_s = N\lambda_s$ are recorded in Table 3.5. $N = 3.2$ Mc/s

Table 3.5 : ULTRASONIC VELOCITIES IN LIQUIDS

Liquid	Molecular Formula	d in cm.	λ_s in cm.	$V = N\lambda_s$ in meters Expt.at 28°C.	Ref.at 24°C.
Water	H_2O	0.140	0.0471	1507	1494
O-Xylene	$C_6H_4(CH_3)_2$	0.162	0.0407	1302	1352
Carbon-tetra chloride.	CCl_4	0.240	0.0275	900	928.5
Butyl alcohol	$CH_3(CH_2)OH$	0.166	0.0400	1280	1315
Transformer Oil.	$C_n H_n$	0.150	0.0440	1400	1425
Glycerine	$C_3H_5(OH)_3$	0.106	0.0622	1990	1986
Nitro-benzene	$C_6H_5NO_2$	0.140	0.0471	1507	1490

The velocity values obtained by Parthasarathy[6] using ultrasonic waves of frequency 7.32 Mc/s is recorded as reference value. The velocity in transformer oil, however, is that given by Babikov.[7] Parthasarathy[8] measured velocity in a large number of organic liquids and observed that it is greater in aromatic compounds than in aliphatic ones. For the former, the range is 1300 m/sec. and above at 25°C, while for the latter compounds 1300 m/s is about the upper limit. In the liquids used above, xylene and nitro-benzene, are aromatic compounds whereas glycerine, CCl_4 and butyl alchohol are aliphatic ones. Transformer oil is a mixed compound and water is inorganic. The results in general are in agreement with the conclusions of Parthasarathy except in the case of glycerine which, in spite of being an aliphatic compound, has a large sound velocity.

3.14 INTENSITY OF ULTRASONICS

The average intensity of ultrasonic waves was calculated by the calorimetric method described in 2.2, in which the rise in temperature of the liquid through which these waves propagated for a definite time was noted. These results for the plane and focussing peizo-electric crystals and for the magnetostrictive transducer are recorded below.

(A) PLANE CRYSTAL

Weight of the copper container	250 gm.
Weight of copper container + 200 cc of transformer oil.	430 gm.
Initial temperature	29°C
Final temperature	30°C
Interval through which waves propagated	10 min.
Frequency of the waves	3 MC/s
Applied voltage across the crystal	70 volt.
Piezo-electric crystal Material	PZT-2
Diameter of silvered region	1.8 cm.
Crystal thickness	0.8 mm.
Specific heat of copper	0.1 cal/gm/c.
Specific heat of transformer oil	0.54 cal/gm/C.

Calculations:

Total power output by the crystal	= JH
	= 10.0 watts.
Area of the radiating surface	= 5.0 $cm.^2$
Average intensity	= 2 $watts/cm^2$

The average intensity of ultrasonic waves of frequency 1MC/s emitted by the 2 cm. PZT-2 crystal, when the applied voltage was 50 was about 2 $watts/cm.^2$ The average intensity of ultrasonic waves of frequency 3 Mc/s emitted by the 1 cm. diameter

PZT-4 crystal was similarly calculated, and was 2.5 watts/cm.^{2} when the applied voltage was 100 across the crystal.

(B) FOCUSSING CRYSTAL:

The ceramic crystal in the shape of a bowl was used to produce intense ultrasonic waves.

Frequency of the waves	= 450 Kc/s
Voltage across the crystal	= 23 volts
Mass of water	= 600 gm.
Water equivalent of the vessel	= 20 gm.
Time interval	= 300 sec.
Rise in temperature	= 5° C.
Specific heat of water	= 1 cal/gm/°C.
Total ultrasonic power	= work per sec = 45 watts

The total ultrasonic power given to water from the concave surface is 22 watts. If this power is concentrated in a very small region then the intensity at that point will be more than 22 watts/cm.^{2} Intensity in the focal region (I_F) was calculated as described below.

The intensity at the focus I_F will be large, Fig 1.1B because all the beams will be focussed at that point. The lateral width of the focal spot will be given by the

same directivity function as in equation 1.1 which controls the beam width of a circular piston source, namely $\frac{2J_1(X)}{X}$ where $X = Ka\sin\theta$. The main lobe carries 84 % of the total energy and is surrounded by many side lobes. The radius γ_F of the circular cross section of the main lobe in the focal region is given by

$$\gamma_F = \frac{3.83}{2\pi} R \frac{\lambda}{a}$$

where R is the radius of curvature and a half the aperture. If the total power output by the transducer is W watts then the average intensity of the main lobe in the focal region will be

$$I_F = 0.84 \, W / \pi r_F^2$$

Substituting the values in Art. 2.11B and Art. 3.13, $r_F = 0.61 \frac{R\lambda}{a}$

$$= 0.28 \text{ cm.}$$

Hence

$$I_F = \frac{0.84}{0.25} \times 22$$

$$74 \text{ Watts/cm.}^2$$

On passing ultrasonics in water a small fountain was formed in the focal region and intense ripples and sonolumini-scence could be observed over a circular

region of diameter about 1.6 cm. and area 2 $cm.^2$ So the corresponding average energy will be

$$I_{av} = \frac{0.84}{2} \times 22$$

$$= 9 \text{ watts/cm}^2.$$

(C) MAGNETOSTRICTIVE OSCILLATOR :

Low frequency intense ultrasonic waves were obtained using a magnetostrictive oscillator. The average intensity of the waves was estimated by the calorimetric method described in 2.2. The readings are given below :

Frequency	= 20 KC/s
DC Voltage	= 12
RF Voltage	= 120
Weight of water	= 200 gm.
SP heat of water	= 1 cal/gm/.°c
Weight of copper calorimeter	= 100 gm.
SP heat of copper	= 0.1 cal/gm/.°C
Time interval	= 300 Sec.
Rise in temperature	= $2^{o}C$
Total ultrasonic power	= work per sec.5.9watts
Radius of the Stub	= 0.5 cm.
Average intensity	= 7.5 Watts/Cm^2

3.15 EXPOSURE TO ULTRASONICS:

Since the attenuation of ultrasonic waves in air is very high it was necessary to use a liquid to transmit ultrasonics from the crystal to the film. The crystal could not be immersed in water because water is a good conductor of electricity. Xylene or transformer oil could be used. It was necessary to pre-moisten the film to obtain ultrasonographs on dry films immersed in xylene or transformer-oil. Xylene evaporates rapidly and has a bad odour. Transformer oil is easily available and is more economical. But this oil has the disadvantage of staining a pre-moistened film. So the crystal was kept in this oil and the film was kept in a test-cell containing water and the optimum a) distance between the crystal and the film; b) angle of inclination of the film and c) time of exposure were determined.

(A) DISTANCE :

The distance from the crystal beyond which Fraunhoffer diffraction or far-field pattern will be observed was calculated by the formula 1.1. This distance = $\frac{a^2}{\lambda}$, and will be 11.3 cm for the 2 cm. diameter crystal in transformer oil, and 2.9 cm for the 1 cm. diameter crystal in xylene. Beyond this distance/

intensity will continuously decrease as $(\text{distance})^2$, neglecting classical attenuation. In the near-field region or Fresnel region there will be central maxima and minima on the beam axis. The distances at which the dark-spot can be obtained by the formula 2.2 ~~and~~ are 1.3, 1.5, 2.2 and 3.7 cm. for transformer oil or water, since the wave length of sound in both these liquids is nearly the same (Art. 3.13). In the experimental arrangement in Art. 2.4A the 2 cm. diameter crystal was immersed in transformer oil and the film immersed in distilled water in the test-cell was exposed to ultrasonics at different distances. The corresponding readings for the density of blackening are recorded in Table. 3.6.

Table 3.6 : DENSITY AT DIFFERENT DISTANCES

Time of exposure	25 minutes
Temperature	27° C
Film	Orwo, panchromatic ASA speed 120

Distance in cm.	Density
1.3	0.20
1.5	0.21
2.2	0.23
2.8	0.20
3.7	0.23
2.20	0.20
2.24	0.21
2.26	0.24
2.30	0.22

The density value for distances in the range 1 to 4 cm. are in agreement with theory. The fact that the density at various distances in the region 2.2 to 2.3 cm. remains practically the same indicates that position of the film is not very critical. This suggests that the acoustic processes which give rise to blackening occur at short distances on either side of the liquid film interface . Both these results are in agreement with those reported by Dehn.[9] In all subsequent experiments the film was kept at distance of about 3 cm. from the crystal face.

(B) ANGLE OF INCLINATION:

Films were exposed for 25 minutes at 27°C and at different angles to the direction of the incident ultrasonic waves of frequency 3 Mc/s and average intensity 3 Watts/cm^2. An image could easily be obtained when the angle of inclination θ was zero, i.e. emulsion layer on the film was parallel to the crystal face and no image could be obtained if the film was rotated by 90°. The density of blackening corresponding to $\theta = 0°$, 30° and 90° was 0.26, 0.06 and zero respectively In all subsequent experiments angle θ was kept zero.

(C) EFFECT OF EXPOSURE TIME:

The density of blackening when the film was exposed to waves of frequency 3 Mc/s and of average intensity 3 watts/cm^2, for 15 minutes at 27^{o}C was 0.08. Images could not be observed for exposure periods of less than ten minutes. The density of blackening increased with increase in exposure time and it was 0.26 for 25 minutes exposure. Larger exposure periods were not possible as the temperature of the test liquid rose rapidly and beyond 30^{o}C the emulsion layer separated from the film-backing. In all subsequent experiments films were exposed to ultrasonics for 25 minutes.

3.16 ERRORS :

The error in the values for the density of blackening are due to (i) Small variation in temperature; (ii) Fluctuation in the output power from the RF oscillator; (iii) Uncertainty in the reproducibility of position of the film and in photographic development and (iv) Non-uniformity in the blackening of the image. The probable error calculated from density values for four identical exposures comes out to be ± 8 %.

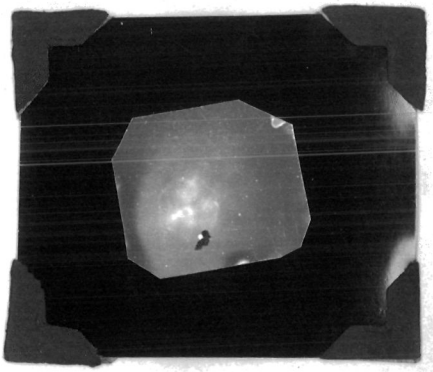

Fig.3.2 An Ultrasonograph(+)

In most cases ultrasonographs were obtained by immersing the film in distilled water and so the images were faint. The intensity distribution in the cross-section of the incident ultrasonic beam was not the same at all distances and so the distance between the crystal and the film was kept constant. The image consisted of a dark spot surrounded by fainter spots (Fig. 3.2) The exposures were repeated atleast twice. The optical density was measured at different points of the dark spot and the average value has been recorded.

3.2 ULTRASONOGRAPHS :

This Article contains the details on the ultrasonographs obtained varying such parameters as transmitting and moistening medium, intensity of ultrasonic waves, temperature of the medium and speed of the film.

3.21 EFFECT OF THE TRANSMITTING MEDIUM:

(A) EXPOSURE TO PLANE CRYSTALS :

Since attenuation of ultrasonic waves of frequency 3 Mc/s is very large in air, a liquid had to be used to transmit ultrasonics between the crystal

and the film. No blackening could be seen if a dry film was immersed in xylene and exposed to ultrasonic waves. However, the film got blackened if it was pre-moistened in water.

(B) EXPOSURE TO FOCUSSED WAVES:

Films were immersed in water and exposed to waves of large intensity obtained from the spherical bowl as described in Art.2.8. The waves emitted by the bowl were focussed just below the surface of water column and the average intensity of the waves in the focal region was 9 watts/cm.^{2}

Sono-luminisfence could be observed by the dark-adapted eye. Films were exposed for one minute by keeping the film (1) at the surface of water so that the film got moistened and (2) just above the surface of water such that the dry film was in air. The films got blackened over a circular region of 4 cm. diameter and the densities of blackening were 0.48 and 0.40 respectively. These results suggest that (1) sonoluminiscence is mainly in the visible region of the spectrum for which the film was sensitised and (2) even a dry film gets blackened if the intensity of sonoluminiscen in the transmitting medium is large.

(C) EXPOSURE TO MAGNETOSTRICTIVE OSCILLATOR:

Using the experimental arrangement described in Art. 2.4 ORWO film of speed 120 ASA was exposed to the stub of the transducer by keeping the film in air at a distance of 3 millimeters and a temperature of 28°C for 5 minutes. Both dry film and film pre-moistened in water were exposed. No image was formed. However if there was a water column in between and the film was exposed at the same distance an image was readily formed. The density of blackening for five minutes exposure was 0.20. If the film was replaced by a long water column and standing waves were allowed to be formed luminiscence could be seen by the dark adapted eye at the end of the stub and in the water column at distances separated by about 7 cm. which is equal to half the wave length of sound waves in water.

The intensity I of the waves in air at a distance $x = 3$ mm can be calculated from the formula[1] $I = Ioe^{-2\alpha x}$ where $Io = 7.5$ watts/Cm^2 and α, at a frequency of 20 Kc/s $\simeq 10^{-4}$ cm^{-1}. The value of I thus obtained will be $\simeq$ Io. The absence of blackening for exposures in air is due to absence of cavitation in air. This stresses the need of a liquid transmitting medium between the crystal and the film.

3.22 EFFECT OF THE MOISTENING MEDIUM:

Dry films immersed in xylene were exposed to ultrasonic waves of frequency 3 Mc/s and of average intensity of 2 watt/cm^2 at 27^{o}C. One cm. diameter PZT - 4 crystals were used such that films could be exposed upto 70 minutes without causing considerable rise in temperature. But no image was formed on the film. However, an image was formed if the film was pre-moistened in water and then exposed to ultrasonic waves. These results are recorded in Table 3.7.

Table 3.7 : EFFECT OF PRE-MOISTENING AND EXPOSURE TIME ON BLACKENING

Time in Minutes		Density of Blackening
Pre-moistening	Exposure	
Nil	70	Nil
2	40	0.06
2	70	0.20
0.1	40	Nil
0.1	70	0.05

These readings indicate that the blackening of the film not only depends on whether the film is pre-moistened or not but also on the amount of pre-moistening.

Marinesco[10-12] and others[13] could not observe any blackening when dry photographic plates immersed in CCL_4 were exposed to ultrasonics but observed the blackening if the plates were pre-moistened in water. Since both the collision process and the density of blackening are enhanced if the film is pre-moistened in water, they concluded that the blackening is due to the collision excitation energy supplied by the incident ultrasonic waves.

Different liquids were taken in the test-cell in which the films were exposed to ultrasonic waves of frequency 3Mc/s. The corresponding densities of blackening are recorded in Table 3.8.

Table 3.8 : BLACKENING OF THE FILM IN DIFFERENT LIQUIDS

Film orwo, panchromatic, 120 ASA speed.

Temperature $27^{o}C$

Exposure 25 minutes.

Liquid	Blackening density
Tap-Water	0.21
Distilled water	0.25
Tap-water & CCl_4 (0.5% of volume)	0.35
Tap-water & ether (20% by vol.)	Nil
CCl_4	Nil
Xylene	Nil
Glycerine	Nil
Nitro-benzene	Nil
Butyl alchohal	Nil
Iso-amyl alchohal	Nil

Pinoir and Pourdier[13] observed that blackening increases when luminol was added to water and decreases on addition of tetrazine to water or on reducing ambient pressure. As addition of luminol to water is known to suppress sonoluminiscence, they concluded that blackening is due to sonoluminiscene and any blackening that might have been produced in the absence of sonoluminiscenee is due to the activity of the medium or due to some chemical reaction in the liquid induced by ultrasonics. Later Polotoskii[14] observed that when ambient pressure is decreased to 100 mm of Hg or increased to 4200 mm Hg sonoluminiscence intensity decreases and blackening disappears.

Our results are in agreement with those of Marinesco[11] and of Pinoir and Pouradier[13]. In all those liquids in which there was no blackening of the emulsion the films were later exposed to faint extemnal light. The films did get blackened indicating that the liquids did not destroy the image that might have been produced.

3.23 INTENSITY EFFECT :

The average intensity of ultrasonic waves that produced a faint image of density 0.05, at 27°C for an exposure period of 25 minutes was about 1.7 watts/cm^2

for ultrasonic waves of frequency 3Mc/s and 1 watt/cm^2 for those of frequency 1Mc/s. This intensity value is of the same order of magnitude as of the one corresponding to the threshold of cavitation in tap-water[4] which is 0.62 and 1.65 watts/cm^2 for ultrasonic frequencies of 0.66 and 2 Mc/s resply. This suggests that the blackening is produced only on the onset of cavitation.

With a gradual increase in the intensity of the waves the density of blackening increased and it was 0.26 when the intensity was about 3 and 2 watts/cm^2 for waves of frequency 3 and 1Mc/s respectively.

3.24 TEMPERATURE EFFECT:

Films were immersed in distilled water maintained at different temperatures inside the test-cell. The change in temperature during the exposure was less than 2^{o}C. The average temperature and the corresponding density values are recorded in Table 3.9. Frequency = 3Mc/s.

Table 3.9 : BLACKENING AT DIFFERENT TEMPERATURES

Temperature in ^{o}C	Density of Blackening
18	Nil
20	0.05
22	0.12
25	0.24
28	0.26

No image could be obtained below $20^{o}C$ using ultrasonic waves of intensity about 3 watts/cm^{2}. However, Marinesco[12] did obtain images at temperatures as low as $4^{o}C$ using very intense ultrasonic waves. He calculated in detail the change in temperature of the liquid due to adiabatic compression accompanying the passage of ultrasonics. This change was bout $0.01^{o}C$ and Zero at $4^{o}C$ and this being very small he concluded that image formation is not due to thermal effect of ultrasonics. However he did not account for the rise in temperature of the emulsion itself on absorbing ultrasonic energy. This rise in temperature in the present investigation could not have been more than $10^{o}C$ in any case, since when a film is immersed in hot water, the emulsion

starts seperating from the backing at 30°C in the presence of ultrasonics and at 42°C in the absence of ultrasonics. Benett[15] too could not obtain an image beyond 30°C as the emulsion separated from the film-backing. Pinor and Pouradier,[13] and later Arkhangelskii,[16] reported that the blackening at 4°C by very intense ultrasonic waves even in the absence of sonoluminiscence is due to chemical action between the liquid and the emulsion.

The above readings are plotted in Fig. 3.1 (a) and the density is found to increase with temperature. However there is a bend in the graph around 25°C. The rate of increase of density with temperature is more in the range 18 - 26° C than in the range 25 to 28°C. Benett[15] working in the region 20 - 26°C observed a linear increase in density with temperature. He used this result to oppose the secondary effect theory of blackening and to support the direct action theory. He said sonoluminiscence[17,18] intensity is known to be decreasing with increase in temperature and if blackening was due to sonoluminiscence, the density should have decreased with increasing temperature.

3.25 EFFECT OF THE SPEED OF THE FILM:

Orwo films of different speeds were immersed in distilled water and exposed to ultrasonics at 27°C. The readings are recorded in Table 3.10. Frequency = 3 Mc/s. Intensity 3 watts/cm² Time = 25 minutes

Table 3.10 : VARIATION OF BLACKENING WITH SPEED OF THE FILM

Speed in ASA	Density of Blackening
125	0.26
400	0.20

Benett[15] had exposed films of different speeds in the range 8 to 120 ASA and observed that the density of blackening was practically independent of the speed. If blackening was due to sonoluminiscenee, he argued, then films of higher speed should have produced denser images. Above results indicate that films of lower speed are more sensitive to ultrasonics. In general the films of lower speed have smaller grains and higher concentration then those in fast films. So our results suggest that emulsions having smaller grains and higher concentration of grains give better results.

It was observed that photographic papers give better results than films. The density of their blackening could not be measured by the transparent densitometer. But a detectable image could be formed even when the exposure time was only 5 minutes. Dehn[9] had obtained similar results and explained them on the basis that paper emulsion absorbs more energy and causes more blackening. More blackening on the paper is probably due to (1) Smaller grain size (2) thicker emulsion layer (3) porosity of the paper backing and (4) higher absorption of energy.

3.3 SONOLUMINISCENCE MEASUREMENTS:

Intense ultrasonic waves propagating through certain liquids produce luminiscence in them. The intensity of this sono- luminiscence in different liquids and at different temperatures has remained controversal (Art 1.3). So these values were independently estimated.

Ultrasonographs were obtained using crystals of frequencies 1MC/s and 3 MC/s and sonoluminiscence measurements have been made using a crystal of 450 Kc/s. However it has been reported that the frequency dependence[19] of sonoluminiscence intensity is due to the frequency dependence of the thresold of cavitation and the relative variation in sonoluminiscence intensity will be the same at different frequencies.

3.31 SONOLUMINISCENCE INTENSITY IN DIFFERENT LIQUIDS:

Galvanometer deflections which are proportional to the intensity of sonoluminiscence in the liquid were noted for different applied voltages accross the crystal at a room temperature of 28 °C. The readings for different liquids are tabulated in Table 3.11.

Table 3.11 : SONOLUMINISCENCE FLUX IN DIFFERENT LIQUIDS

Liquid	Voltage across the crystal.	Galvanometer deflection in mm. d (i)	(ii)	(iii)	Mean d
Tap-Water	0	19	19	19	19
	8	19	19	19	19
	10	19.	20	20	20
	12	22	21	22	22
	15	23	22	23	23
	17	28	29	26	28
	20	40	38	35	38
	22	44	43	44	44
Distilled-Water	0	19	19	19	19
	8	19	19	19	19
	10	20	20.	20	20
	12	24	25	25	25
	15	35	33	36	35
	17	43	40	46	43
	20	50	51	53	51
	22	69	66	64	66

Table 3.11 (Continued)

Liquid	Voltage accross the crystal	Galvanometer deflection in mm. d			Mean d
		i	ii	iii	
Carbon-Tetra Chloride- CCl_4	0	19	19	19	19
	8	19	19	19	19
	10	19	19	19	19
	15	19	20	20	20
	20	19	22	12	22
	25	24	23	24	24
Tap water + CCl_4 (0.5% by volume).	0	19	19	19	19
	10	19	19	19	19
	12	27	29	30	29
	15	37	39	37	38
	18	50	64	50	51
	21	79	74	81	78
Tap-water + CCl_4 (20% by volume)	0	19	19	19	19
	10	19	19	19	19
	15	22	21	23	24
	20	26	25	25	25
	22	28	27	27	27

Table 3.11 (Continued)

Liquid	Voltage across the crystal	Galvanometer deflection in mm. d			Mean d
		i	ii	iii	
Tap-water + Ether (20% by volume)	0	19	19	19	19
	10	19	19	19	19
	12	19	19	20	19
	15	20	21	21	21
	18	20	21	22	21
	22	23	23	24	23
Glycerine	0	19	19	19	19
	10	19	19	19	19
	15	20	20	21	20
	18	22	22	22	22
	20	25	24	26	24
	22	27	28	27	27
Butyl-alchohol	0	19	19	19	19
	10	19	19	19	19
	15	20	21	20	20
	18	21	22	21	21
	20	21	22	23	22
	22	23	23	24	23

CCl_4 showed little sonoluminiscence. Similarly nitrobenzene, ethyl ether, Xylene and transformer oil showed little or no sonoluminiscence for input voltage upto 22. Butyl and iso-amyl alchohols exhibited less sonoluminiscence than water.

Chamber's[17,18] studied sonoluminiscence in many liquids, visually. He found that when a solution of polar substance in a non-polar solvent viz. water in CCl_4, was irradiated, the luminiscence intensity depended on the concentration of the dipoles in the liquid. He advanced an empirical law that the intensity of sonoluminiscence in pure liquids is directly proportional to the product of coefficient of viscosity and the molecular dipole moment of the liquid. Jarman[20] studied sonoluminiscence in many other liquids and his results showed that the above rule is not always true. He said that sonoluminiscence intensity is directly proportional to the square of the surface tension of the liquid and inversly proportional to the vapour pressure of the liquid. Some physical constants[21] of these liquids and their sonoluminiscence fluxes are given in Table 3.12.

Table 3.12 : SONOLUMINISCENCE FLUX AND SOME PHYSICAL CONSTANTS OF CERTAIN LIQUIDS

Physical Constant	Water	Butyl alchohol	Glycerine	CCl_4	Ether	Xylene	Nitro Benzene
Vapour pressur (P) at 25°C mm Hg	24	12	1	41	537	6.6	1
Surface Tension (T) at 20°C dynes/cm.	73	23	63.4	26.5	17.01	30.02	43.9
Dipole Moment at 20°C	1.87	1.72	-	0.60	1.22	0.51	3.90
Viscosity X 10^{-3}, poise at 30°C	0.80	2.88	629	0.96	0.226	0.69	2.01
$\frac{T^2}{P}$	222	44	4000	17	0.5	136	2000
Sono-luminisence Flux in mm	47	4	8	3	3	4	Nil

The above results contradict the conclusions of Jarman and of Chambers. No single rule concerning the sonoluminiscence intensity of liquids to their physical constants is in sight.

Chambers observed intense sonoluminiscence in glycerol and nitrobenzol but many have observed only a very weak sonoluminiscence in water free glycerine and nitrobenzol.[22,23] Water free nitro-benzol showed no sonoluminiscence, but glycerine emitted faint sonoluminiscence in the present investigation.

Prudhomme[24,25] observed that the sonoluminiscence intensity in water increased in the presence of CCl_4 though CCl_4 by itself did not emit sonoluminiscence. He said that ultrasonic waves disperse droplets of CCl_4 in irradiated water which facilitates cavitation and thereby increases sonoluminiscence. Jarman too obtained similar results, and he has remarked that molecules of CCl_4 which is a non-polar organic substance form cavities of a particular kind in the tetrahedral structure of water and thereby reduces it tensile stress to favour cavitation. Another explanation[26] has also been suggested. The molecules of CCl_4 penetrate into the cavitation bubble and undergo ionisation followed by interaction with H and OH molecules of water or with excited molecules of gases in the bubble. These reactions favour the chemical and physical processes in the cavitation bubble, and enhance sonoluminiscence.

Ethyl ether suppresses sonoluminiscence in water[27] Frankel[28] explained this by saying that substances with higher vapour pressure than water rapidly distend the cavitation bubble when they penetrate into it and thus create conditions in the cavity which hinder electronic break down and thereby the emission of light.

The sonoluminiscence in distilled water was not-affected by dissolved salts,[29] acids or alkalies like, NaCl, $CaCl_2$, Hcl, or NH_4OH. But the brightness changes[22,29,30] with dissolved gas. There was no sonoluminiscence in water saturated with hydrogen. Probably it is because of dissolved gas that sonoluminiscence intensity in tap-water is less than that in distilled water.

In the intensity region measured above the intensity of sonoluminiscence increased with the applied voltage in agreement with the results of Griffing and Sette[22] and those of Negishi.[30] But working with a similar experimental setup Negishi observed that the intensity of sonoluminiscence increases till the voltage reaches 42 and suddenly drops at higher voltages.

3.42 : SONOLUMINISCENCE FLUX AT DIFFERENT TEMPERATURES

Tap-water was taken in the test-beaker (Art. 2.8), and the galvanometer deflections were noted at different applied voltage across the crystal. Fresh sample of water was used for

each temperature maintained correct to 0.5°C. The readings are tabulated in Table 3.13.

Table 3.13 : SONOLUMINISCENCE FLUX IN WATER AT DIFFERENT TEMPERATURES

Applied Voltage	Galvanometer deflection in mm.					
	18°C	24°C	27°C	30°C	40°C	50°C
0	14	14	14	14	14	14
9	14	14	14	14	15	15
12	16	18	16	16	16	17
15	17	21	19	18	19	18
20	29	37	34	31	28	23
23	43	51	44	46	38	26

Chambers[17,18] and others[29,31] observed that sonoluminiscence is more pronounced at lower temperatures, and with increase in temperature the intensity gradually reduces to zero. But Alfredson[32] observed that sonoluminiscence intensity in distilled water increases with rise in temperature from 3° to 25°C and decreases beyond 25°C. He qualitatively explained this on the basis that with the increase in temperature vapour pressure of water increases and surface tension decreases and the decrease in surface tension facilitates cavitation[20] but excess vapour pressure absorbs sonoluminiscence. The above results which are plotted in Fig.3.1(b) are in agreement with those of Alfredson[32].

3.4 SIMULTANEOUS EXPOSURE TO LIGHT AND ULTRASONICS:

Woeber[33] has reported that the dosage of X-rays required to destroy a tissue in reduced by a factor of two if the tissue is irradiated in the presence of ultrasonics. In case of ultrasonography, Marinesco[10] has reported that pre- exposure to ultrasonics makes the photographic film more sensitive to light. So during the course of this investigation an attempt was made to study this aspect of ultrasonography. The films were exposed to light and ultrasonics for 25 minutes each, simultaneously and separately one after another at a temperature of 27°C and the results are recorded in Table 3.14.

Table 3.14 : BLACKENING OF THE FILMS EXPOSED TO LIGHT AND ULTRASONICS .

Exposure to	Fog	Total Density from Fog + L	Total Density from Fog + L + US	Net Density from ultrasonics
Ultrasonics (US)	0.22	--	0.36	0.14
US + Light (L) (Simultaneously)	0.23	0.63	0.80	0.17
L first and then US.	0.24	0.66	0.85	0.19

When film was exposed to light and ultrasonics, a circular image due to ultrasonics was super-imposed on the blackening caused by light. The blackening due to ultrasonics alone was more if the film was pre-exposed to light or if it was simultaneously exposed to light. This is probably due to the fact that the densities of blackening in the latter cases lie in the linear region of the Characteristic curve of the photographic film. The fact that the net density in the last two cases were nearly the same indicates that the two blackenings are additive and ultrasonics or light do not accelerate the blackening caused by one another.

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C H A P T E R IV

DISSCUSSION

The possibility of the blackening of the photographic film by mechanical, thermal, hydrodynamic and cavitational effects of ultrasonics has been disscussed in the light of the experimental results of this investigation. By taking into account the results on the variation in sonoluminiscence intensity and changes in the emulsion on absorbing water it has been possible to explain all the observed results on ultrasonography on the basis that the blackening is due to cavitational effects. In conclusion a mechanism which attributes this blackening to cavitational effects has been suggested.

4.1 BLACKENING OF PHOTO-EMULSION BY ULTRASONICS

In the present investigation it was observed that when a photographic film was pre-moistened in water or any liquid having sufficient sonoluminiscence intensity, and irradiated by ultrasonics a latent image was formed on it which became visible on development. No image was formed when the film was dry. The blackening of the image increased with the increase in (1) water absorbed by the emulsion (2) sonoluminiscence intensity and (3) exposure time. No image was obtained even on a moist film in the absence of liquid medium between the source and the film. The minimum intensity of the ultrasonic waves required to blacken the emulsion was of the same order as the cavitation thresold intensity (Art. 3.23). Minimum exposure period was about ten minutes which indicates that the image is largely due to the development of silver specks on the surface of the grains. The blackening depended on the temperature of the moistening of liquid and on the speed of the film. The film of lower speed which is less sensitive to light gave better ultrasonographs. The action of ultrasonics on the film is similar to that of light and the effects of the two are additive.

This blackening may be due to one or more of the following ultrasonic effects (1) Mechanical action (2) Thermal effects; (3) hydrodynamic effects and (4) chemical action,

sonoluminiscence etc., accompanying cavitation. In what follows the possibility of blackening by each of the above is discussed.

4.11 BLACKENING DUE TO MECHANICAL ACTION

The excitation energy[1] required to raise an electron from the valence band to the conduction band in the case of silver halide crystals is about 3 eV. (Since 1 eV = 1.6×10^{-12} ergs, 1 watt = 4.2×10^{7} ergs $\simeq 10^{19}$ eV.) It has been reported that an external pressure of about 1000 kg/Cm^2 is required[2] to produce blackening on the photographic emulsion and the corresponding intensity will be about 10^6 watt/cm.^{2} This large pressure variation can be produced by cavitation and not by radiation pressure.

Sound waves being elastic waves carry energy with them and this phonon energy[3] = $\frac{hcq}{2}$ where h is Plancks constant, c is the velocity of sound and q = π/a, a being the interatomic distance. The maximum energy associated with a phonon, corresponding to h = 4.1×10^{-15} eV, c $\simeq 10^5$ cm/sec and a $\simeq 10^{-8}$ cm will be about 0.01 ev. Both the above arguments indicate that the probability of blackening by mechanical excitation is very small.

When a dry film was immersed in xylene and exposed to ultrasonics of intensity of a few watts/cm^2 there was no blackening but it got blackened in if the film was pre-moistened/water.

Similar observation led Marinesco[4] to conclude that blackening is due to mechanical excitation which is favoured in a moist emulsion. However, when the emulsion was premoistened in a mixture of water and ether which showed little sonoluminiscence there was no blackening. Besides, when the premoistened emulsion was exposed to ultrasonic waves of intensity 7.5 watts/cm^2 in air, there was no blackening. Both these observations clearly indicate that blackening is not due to mechanical excitation.

The blackening observed when the film was immersed in developer or water containing a few drops of tetrazine to quench sonoluminiscence and irradiated by ultrasonic waves of intensity of hundreds of watts/Cm^2 was attributed by Pinoir and Pouradier[5] and by Arkangalskii[6] to the enchancement of chemical fogging by the waves. The photographic film on immersion in developer or in water for a very long time gets blackened due to chemical fogging. The above authors were also of the view that blackening is not caused by mechanical excitation. The mechanical action of ultrasonics which can decrease the strength of the emulpion layer due to alternate stresses and strains beyond the elastic limit or mechanical stirring produced by them can only facilitate image formation.

4.12 BLACKENING DUE TO THERMAL EFFECTS

The absorption of the incident ultrasonic energy will raise the temperature of both the transmitting liquid and the

emulsion. The maximum temperature of the transmitting liquid could have been 30°C because beyond this temperature the emulsion layer separates from its backing under ultrasonic irradiation. The maximum temperature of the emulsion itself might have been about 40°C for at around 40°C it starts dissolving in water. However there can be large changes in temperature in microspopic regions in the liquid, but this will be due to cavitation phenomenon. The results in Article 3.11 show that a change in temperature in the range 3 to 45°C does not produce any appreciable change in density. So it is reasonable to assume that a change in temperature up to 10°C due to absorption of ultrasonic energy does not produce the observed blackening. The rise in temperature will only soften the emulsion and this will enhance the hydrodynamic and mechanical effects of the ultrasonic waves.

4.13 BLACKENING DUE TO HYDRODYNAMIC EFFECTS

The hydrodynamic effects due to propagation of ultrasonics in a liquid will produce acoustic streaming and microstreaming. Acoustic streaming produces a forward motion of the liquid molecules and this is more pronounced near the crystal surface. Accoustic microstreaming produces diffusion of the liquid

molecules for a short distance on either side of the surface of separation of the two media of different viscosities. The fact that the density of blackening remains the same over a short distance (Article 3.15) suggests that microstreaming takes part in the blackening phenomenon. As was obvious from the blackening of the film pre-moistened in water and immersed in xylene, microstreaming helps to bring out the water molecules to the surface of the emulsion and to carry the luminiscent bubbles inside the emulsion. The energy gained by the molecules due to their movements in the hydrodynamic process will be too small to provide excitation energy to the silver halide crystals.

4.14 BLACKENING DUE TO CAVITATION

Ultrasonic cavitation in liquids produces (1) pressure changes of hundreds of atmospheres, (2) temperature changes of few hundred degree centigrade (3) shock-waves etc. These secondary effects are responsible for the chemical reactions and luminiscence occurring during the passage of ultrasonics through some liquids.

If a photographic emulsion is immersed in an active medium like developer or in water which has very little activity, for a long time even in the absence of ultrasonic irradiation, it gets blackened due to chemical fogging. Irradiation of the film by ultrasonics is known to accelerate this phenomenon of

chemical fogging. There is no other known chemical reaction which will blacken the film when immersed in water and irradiated by ultrasonics.

A very large change in pressure or temperature and intense shock waves can blacken a photographic emulsion. But the role played by these effects of cavitation in blackening the film is not easily detectable since these effects could not be measured independently, and though they give rise to sonoluminiscence the role played by them individually in doing so is not yet understood.

In the present investigation there was no blackening on the film in the absence of cavitation as was seen in (1) when the film was exposed to intense ultrasonic waves in air and (2) when the intensity of the waves was below the cavitational threshold intensity. There cannot be sonoluminiscence in the absence of cavitation and there was no blackening in the absence of sonoluminiscence or when its intensity was small as was observed in Articles 3.21 and 3.22. Films easily got blackened even when they were kept in air above the liquid surface provided the intensity of sonoluminiscence in the liquid was large (Article 3.21). All these observations support the view that blackening is produced by cavitation. But the results that there was no corresponding change in the density of blackening with the change in (1) speed of the film and

(2) sonoluminiscence intensity in water in the temperature range 18-28°C, apparently contradict the hypothesis that blackening is due to cavitation.

4.2 EXPLANATION OF THE RESULTS

Our results indicate that the blackening of the photographic film is possibly due to ultrasonic cavitation though in some cases the results apparently contradict this hypothesis. These results will be now considered in the light of the results on (1) sonoluminiscence (2) amount of water absorbed (3) size and number of silver halide grains in the emulsion.

4.21 EFFECT OF TRANSMITTING MEDIUM

Our results indicate that ultrasonographs can be obtained (1) if the film on pre-moistening is immersed in a liquid medium and (2) on a dry film if the transmitting liquid exhibits intense sonoluminiscence. The results on exposure of films to magneto-strictive oscillations (Art. 3.21) show that the mere absorption by the film of a liquid ~~by~~ capable of emitting solonoluminiscence is not sufficient to blacken the film, and that it is necessary to have a liquid column infront of the film. Cavitation can hardly take place inside the emulsion but it is favoured at the

liquid film interface. The luminiscent bubbles produced in cavitation blacken the film. So the results stress the necessity of the phenomenon of cavitation in producing ultrasonographs.

4.22 EFFECT OF MOISTENING LIQUID

The absence of blackening in a film immersed in a non-moistening liquid (Art. 3.22) can be explained by the fact that (1) the intensity of sonoluminiscence in the transmitting liquid was small and (2) only the silver halide grains on the surface of the emulsion could get exposed to cavitational effects. An image could be obtained in the moistened film because then (1) the moistening liquid produced sufficient luminiscence and (2) the silver halide grains inside the emulsion also got exposed to luminiscent bubbles brought inside the emulsion by microstreaming and cavitational processes. These views are also supported by the fact that (1) there was no image in a moistened film when the moistening liquid (like water + ether) exhibited little sonoluminiscence (2) even a dry film kept in air got blackened when the sonoluminiscence intensity of the transmitting liquid was large (3) absorption of more water produced more blackening and (4) the blackening was proportional to the intensity of sonoluminiscence in the moistening liquid.

4.23 INTENSITY EFFECT:

The density of blackening at different distances along the axis of the plane crystal (Art. 3.15) corresponds with the intensity distribution of the diffraction pattern of the emitted waves (Art. 1.31). The film got blackened in all those positions where the resultant intensity was large. The blackening was same for short distances on either side of the peak position and this is probably due to the fact that microstreaming occurs for short distances on either side of the surface of separation of two media of different viscosity

The decrease in blackening when the film was inclined at an angle to the normal to the beam axis is due to (1) The decrease in the number of points of constructive interference near the surface of the emulsion and these points have higher intensity of ultrasonics and luminiscence, (2) decreas in the radiation force which will reduce the mechanical and hydrodynamic effects.

The results that no blackening could be obtained if intensity of waves is below their cavitation threshold intensity of the waves stress the necessity of cavitation to blacken the film .

4.24 TEMPERATURE EFFECT:

As the temperature increases (1) the emulsion absorbs more water (Art.3.12) and (2) the intensity of sonoluminiscence in water increases till about 24°C, beyond which it decreases (Art 3.32). There was no blackening in case of any of the non-acqueous solutions that were used. These factors explain the increase in blackening with temperature in the range 18 to 28°C and also the bend in the curve (Fig. 3.1a) density of blackening against temperature. Though in general the increase in temperature increases the mobility of silver ions in the crystal, rise in temperature of about 10°C would not produce any change in the density of blackening (Art. 3.11).

4.25 SPEED EFFECT:

Though in general a film of lower speed is less sensitive to light than the one having higher speed it was observed that the density of blackening of ultrasonographs was more on films of lower speed value (Art.3.26). Apparently this contradicts the hypothesis that blackening is due to sonoluminiscence. This can be explained by the fact that (1) the sensitivity of the films decrease on absorbing water (Art. 3.11) and (2) the films of lower speed contain grains which are less oblong and more

in number than the one with higher speed and this influences blackening as follows. The speed of the emulsion øis governed by the chemicals added to it and by the number and size of the silver halide grains. The grains in the slower emulsion are smaller in size but more in number. Average grain-size, average thickness and average number of grains per milli-liter corresponding to ASA speeds 150 and 450 are 0.8μ, 0.18μ, 0.63×10^9 and 1.4μ, 0.23μ, 0.17×10^9 respectively.[7]

Though in general the silver halide crystals are cubical in shape, inside the emulsion their shape varies. Assuming the grains to be cylinderical tablets the average total surface area of grains in the slow and fast emulsions will be $1.6\mu^2$ and $3.6\mu^2$ whereas their areas of projection will be $0.6\mu^2$ and $1.6\mu^2$ respectively. Ordinarily only the front surfaces of thegrains in the outermost layer are exposed to light[8] but when exposed to ultrasonics all the sides of grains contained in different layers of the moist emulsion can get exposed to light. Since (i) the ratio of the total surface area to the projection area is larger in smaller grains and (ii) the ratio of the total number of grains in the emulsion to that on the surface of the emulsion is also larger when grains are smaller in size, the density of ultrasonographs in the slow emulsions will be proportionately more than when exposed to light.

4.3 DISCUSSION ON THE MECHANISM:

Marinesco[4] auggested that blackening is caused by the shock action of ultrasonic waves. This direct action theory, however, cannot explain (i) the variation in the density of blackening with ambient pressure[5,9] (ii) the variation in the density of blackening of films immersed in tap-water, distilled water, tap-water containing few drops of CCl_4 or in tap-water containing few drops of ether and (iii) the fact that no blackening is produced when a moistered emulsion is exposed to intense ultrasonic waves in air[5]. Earlier attempts to attribute the effect to sonoluminiscence were not completely successful[10] as they could not satisfactorily account for (i) the variation in the density of blackening with the speed of the film and (ii) the increase in the density of blackening with temperature.

On the basis of the experimental work under report, the following mechanism is suggested which assumes blackening as being due to cavitation and

and overcomes the limitations mentioned above.

As is well known ultrasonic waves propagating through liquids give rise to the phenomenon of cavitation[11] which produces intense shock-waves, electrical micro-discharge, localised and large pressure and temperature rises, chemical action and sonoluminiscenee. It is estimated that pressure may change by thousands of atmospheres and temperature by few thousand ^{o}C. Cavitation is enhanced in the presence of external nuclii, minute dust particles, absorbed gas, and in the presence of solid particles if they are not wetted by the liquid or if they contain cracks or pores such that gas particles may be trapped between the solid and the liquid phases. The thickness of the emulsion layer of the film is about 6μ. The size of most of the silver halide grains in the emulsion range from 0.1μ to 2μ. They are very scarcely soluble in water and within the emulsion they are covered by an adsorption layer of gelatin. Gelatin constitutes the major portion of the photographic emulsion. It is a complex organic compound which is highly porous. So when a moist emulsion is irradiated by ultrasonics

the silver halide grains with an adsorption layer of organic matter and porous gelatin can provide ample entrapped gas molecules to serve as nuclii for cavitation.

Cavitation occurs at the liquid-film interface. It is evident from the blackening of the moist emulsion immersed in xylene, that there is microstreaming in the immediate vicinity of the surface separating the two phases. This suggests a mechanism of blackening in which silver halide grains are excited or dissociated due to optical effect of large number of luminiscent microbubbles which surround them. The difference between a moist emulsion exposed to ultrasonics and the one that is exposed to light is that, in the former all the sides of the grains embedded in different layers within the emulsion are exposed to light whereas in the latter only the front surfaces of the grains in the outermost layer are exposed to light. The mechanical action of ultrasonics which can decrease the strength of the emulsion layer due to alternating stresses and strains beyond the elastic limit, the hydrodynamic action of microstreaming, and the heating of the emulsion by absorbed ultrasonic energy will facilitate the image formation by cavitation.

On the basis of the mechanism herein suggested the limitations stated earlier can be satisfactorily explained. So far as the variation in the density of blackening with

pressure is concerned results of Polotoskii[9] and others clearly show that the variation of sonoluminiscence intensity with pressure corresponds to the variation in density of blackening with pressure. Our sonoluminiscence intensity measurements show that the intensity in different liquids correspond to the optical densities of blackening of films immersed in those liquids. There is no image on the film exposed to ultrasonic in air because of the absence of the phenomenon of cavitation in air. The result that the density of images do not decrease with the decrease in the speed is explained by the facts (i)all the sides of the silver halide grains are exposed to light and the thickness of the smaller grains are proportionately more and (ii) even the grains inside the emulsion are exposed to light. The variation in density of ultrasonographs with temperature is explained by the facts that (i) the sonoluminiscence intensity in water increases with the increase in temperature upto 24°C and (ii) the sonoluminiscence intensity increase with temperature on account of increased amount of water absorbed at higher temperatures.

So it is found that all the experimental results on the blackening of photographic emulsion by ultrasonics obtained in the present investigation and those reported previously by other workers can be explained on the basis that blackening is due to secondary effects accompanying cavitation.

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A B S T R A C T

of the thesis entitled

"EFFECT OF ULTRASONICS ON PHOTOGRAPHIC FILMS"

Ultrasonic waves are mechanical waves of frequency greater than 20KC/s unlike light waves which are electromagnetic in nature. When a moist photographic film is exposed to ultrasonic waves it gets blackened even in the absence of light. The mechanism by which ultrasonic waves blacken the photo-emulsion has remained controversial. Many theories have been suggested prominent among which are the direct action theory which attributes blackening to collision excitation energy due to incident ultrasonic waves and the secondary action theory which attributes blackening to luminiscence produced in certain liquids when intense ultrasonic waves propagate through them. The present work is an attempt to understand this mechanism. The details of this investigation are described in this thesis consisting of four chapters namely Introduction, Experimental, Results and Discussion.

The first chapter begins with a detailed up-to-date review of the experimental results on the blackening of photo-emulsions by ultrasonics in which the various theories on blackening and their contradictions are discussed. This is followed by a brief description of the nature of the photo-

emulsion, production of latent image in it .. and on the development of this image. Certain ultrasonic phenomena like the radiation pressure in front of a plane crystal and the phenomenon of ultrasonic cavitation have been briefly described. Sonoluminiscence accompanying ultrasonic cavitation and the contradictions in its origin and in its intensity values in different liquids and at different temperatures are disscussed. The problem and the various experiments that will be performed to solve it are stated at the end of the first chapter.

The experimental details are given in the second chapter. Ultrasonic waves were obtained using peizo-electric crystals of frequency 0.45, 1 and 3 MC/S and magnetostrictive transducer of frequency 20 KC/S. Experimental details to measure the wavelength and intensity of ultrasonics are described. The details of the construction ofan RF oscillator of input power 100 watts and of frequency range 1 to 5 MC/S and of an optical densitometer to measure the film blackening are described. The details of the assembly of the apparatus to obtain ultrasonographs using peizo-electric and magnetostrictive transducers are illustrated. The experimental arrangement to measure sonoluminiscence intensity using a peizo-electric ceramic bowl of frequency 450 KC/S and a photomultiplier tube is also illustrated. The experimental procedure to estimate the change in weight and volume of the film on absorbing water and the effect

of temperature and humidity on the blackening of the film is given in the end of the second chapter.

The details of the results obtained in this investigation are given in the third chapter. The densities of blackening of the ultrasonographs obtained by varying such parameters as, (i) distance and angular position of the film; (ii) intensity and frequency of the waves (iii) moistening of the film in different liquids; (iv) speed of the film; (v) temperature;(vi) transmitting medium;(vii) presence of external light,etc. are recorded. Whereas in most of the previous investigations the films were immersed in dilute developer in the present work they have been immersed in distilled water. The density is found to increase with the increase in (i) intensit of the waves; (ii) time of exposure; (iii) pre-moistening of the film;(iv) sonoluminiscence intensity;(v) temperature and i is found to decrease with the increase in (i) angle between the normal to the film and the direction of the incident waves and (ii) speed of the film. These results have been compared with those of the previous workers. The intensity and wavelength of the ultrasonic waves have been measured. The relative values of the sonoluminiscence intensity in water, xylene alchohal,carbon tetra chloride, nitrobenzene, glycerine etc. and in case of water at different temperatures are tabulated and compared with the results so far available. The sonolumi-

out 25°c. The

results on the variation of density of blackening of the photographic film exposed to ionising radiation at different temperatures and humidities are recorded. The density of blackening decreased with increase in humidity but it remained the same in the temperature range 3 to 47°c. The amount of water absorbed by the film and the corresponding change in its dimensions are also recorded.

On the basis of these results the possibility of blackening by different ultrasonic effects like mechanical, heating, hydrodynamic and cavitational are discussed in the beginning of the fourthchapter. The results, excepting those on variation of blackening with temperature and film-speed, suggest that the blackening is due to cavitational effects. The results on the blackening of the film are then examined along with those on the sonoluminiscence intensity, water absorption by the film and sensitivity dependence on temperature and size of the silver halide grains. It is then found that the variation in the blackening with all the parameters including temperature and film speed can be explained on the basis that the blackening is due to cavitation. A mechanism of blackening of photographic films by ultrasonics is then suggested. Cavitation is favoured at the liquid film interface because of the air molecules entrapped (1) at the interface; (2) inside the porous gelatin and (3) between the silver halide grains and the adsorbtion layer of gelatin. The cavitational effects like sonoluminiscence act on the silver halide grains on the

surface and in the interior of the emulsion layer unlike ordinary light which act only on the front surface of the grains in the outermost layer. The hydrodynamic, thermal, mechanical and chemical effects of ultrasonics facilitate the image formation by cavitational effects. It is found that all the observed results on the variation of blackening of photo-emulsion by ultrasonics can be satisfactorily explained by this mechanism.